

[Fe(qdt)₂][−] salts; an undimerised Fe^{III} bisdithiolene complex stabilised by cation interactions

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(*n*-Bu)₄N[Fe(qdt)₂] provides the first example of an undimerised Fe^{III} bisdithiolene complex with well isolated square planar coordinated [Fe(qdt)₂][−] units, due to short apical Fe⋯H, Fe⋯C and S⋯H contacts with the cations, while the tetraphenylarsonium salt of this complex presents the usual dimerisation as [Fe(qdt)₂]₂^{2−}, with square-based pyramidal coordination of Fe.

Transition metal bisdithiolene complexes have attracted increasing interest for almost four decades due to rich redox behaviour, unique electrical, magnetic and optical properties with relevance in the fields of materials science, analytical chemistry, catalysis or biological systems.¹ This type of complex is known to exhibit a large variety of coordination geometries, ranging from tetrahedral to square planar, with well isolated [M(S₂X)₂] units or dimerised, trimerised or even polymeric arrangements of these [M(S₂X)₂] units. Square planar coordination geometry is commonly found with metals of the Ni and Cu groups in the anionic form, [M(S₂X)₂][−].

The square pyramidal, 4 + 1, coordination due to the formation of dimeric arrangements, [M(S₂X)₂]₂, is also commonly found especially for M = Fe, Co and to a smaller extent occur also for Ni.^{1,2} Other geometries are also known, for example with Co, where trimerised, [Co(S₂X)₂]₃^{2−,3} and even polymeric, [Co(S₂X)₂]_n^{−,4} arrangements of approximately square planar units have been also described. In spite of several attempts to understand these variable geometries,⁵ the rationale behind this structural diversity was not completely clear, the electronic structure of these type of complexes and the role of the ligands still being the subject of recent studies.⁶

So far, no example of an Fe^{III} bisdithiolate complex has been reported exhibiting a configuration other than the strongly dimerised one, as confirmed by a search of the Cambridge Crystallographic Data Base, indicating for such structures apical Fe–S bond distances in the range 2.44–2.50 Å, only slightly larger than the equatorial distance typically in the range 2.21–2.25 Å. Early work with iron bisquinoxalinedithiolate (qdt) complexes, indicated the occurrence of paramagnetic iron bisquinoxalinedithiolate complexes, but in view of other data, namely ⁵⁷Fe Mössbauer spectroscopy, five-coordination was always assumed.⁷

In this paper we show that Fe(III) complexes with the qdt ligand can, depending on the cation, adopt different coordination geometries (square planar or pyramidal) and we report the first example of a non-dimerised square planar Fe^{III} complex with a perfectly square planar geometry and a *S* = 1/2 spin state; (*n*-Bu)₄N[Fe(qdt)₂]. This geometry contrasts with that of the same complex with the tetraphenylarsonium cation which shows the usual dimerisation of the [Fe(qdt)₂][−] units with the Fe atoms in a 4 + 1 coordination geometry. These two coordination geometries of Fe(III) bisquinoxalinedithiolate demonstrate the role played by Fe⋯C and Fe⋯H short apical contacts toward the cation in stabilizing the square planar S coordination geometry.

(*n*-Bu)₄N[Fe(qdt)₂] (**1**) and (Ph)₄As[Fe(qdt)₂] (**2**) (see Fig. 1), were obtained from quinoxalinedithiol and FeCl₃ using standard procedures.[‡] The crystallisation of these compounds is rather sensitive to the solvent and other conditions used. Although a product with uniform aspect and consistent elemental analysis can be obtained, crystals of a quality suitable for X-ray structure analysis are in general difficult to obtain.

The X-ray analysis of **1** reveals that this compound crystallizes in monoclinic space group *C2/c*. The Fe atom is located at an inversion center and therefore the complex presents a perfectly square planar geometry. The cation has the nitrogen atom placed on a two fold axis.

The [Fe(qdt)₂][−] anion presents several short contacts with atoms both from other anions and cations (Fig. 2).

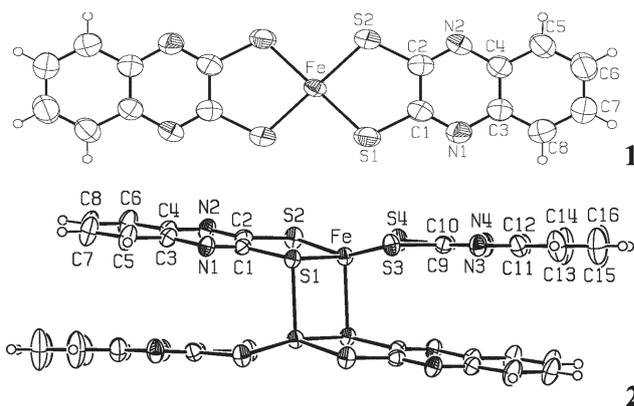


Fig. 1 ORTEP diagrams of the Fe(qdt)₂[−] complexes in **1** and **2**. Fe–S bond lengths in **1** are 2.1729(14) Å and 2.1770(14) Å, shorter than the corresponding basal Fe–S distances in **2**, 2.2259(13), 2.2289(13), 2.2436(13) and 2.2368(12) Å. The apical distance is 2.4884(13) Å. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

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There are hydrogen bonds between the N and H atoms of ligands in neighbouring units, that connect the complexes into two chains along $a + b$ and $a - b$. Most important are two pairs of remarkable short apical contacts between the Fe atom and the C and H atoms from the cations placed above and below the complex. This type of $\text{Fe}\cdots\text{H}$ and $\text{Fe}\cdots\text{C}$ short contact is rather unusual and the former can be seen as resulting from a type of H bond. To the best of our knowledge this is the first time this type of intermolecular $\text{Fe}\cdots\text{H}$ contact has been described and this interaction assists steric hindrance factors in preventing the formation of the apical Fe–S bond typical of the dimerised arrangements.

An important role is played also by a hydrogen bond of two S atoms of the complex towards a different cation; $\text{S2}\cdots\text{H10B}^*$ ($* = x, y - 1, z$) at 2.86 Å. Therefore the S atoms which usually in dimerised species $[\text{Fe}(\text{S}_2\text{X})_2]_2^{2-}$ are involved in a Fe–S apical bond, in this complex are involved in two hydrogen bonds.

The critical role of these Fe–cation interactions in stabilising the rare square coordination geometry is also illustrated by comparison with the crystal structure of a selected single crystal of **2** that is triclinic space group $P\bar{1}$. Here the $[\text{Fe}(\text{qdt})_2]^-$ anions adopt the usual dimeric arrangement with an inversion center located between the two Fe atoms (Fig. 1 and 3) and Fe–S bond lengths typical of the 4 + 1 coordinated Fe(III) bisdithiolene complexes.

The $[\text{Fe}(\text{qdt})_2]^-$ anion in **2** exhibits several short contacts with the cation phenyl rings, namely through the N atoms which are all hydrogen bonded to the cation, at variance with **1** in which the N atoms were instead involved in interanion hydrogen bonds connecting the complexes side by side. One of the phenyl rings is connected through a hydrogen bond $\text{C35}\text{--}\text{H35}\cdots\text{N2}$ at 2.51 Å and a weak hydrogen contact $\text{C34}\text{--}\text{H34}\cdots\text{N3}^*$ ($* = 1 - x, -y, 1 - z$) at 2.67 Å to the two dimerised units.

Clearly, in the structure of **1**, the above described $\text{S}\cdots\text{H}$, $\text{Fe}\cdots\text{H}$ and $\text{Fe}\cdots\text{C}$ contacts between the complex and the cations assist steric hindrance factors that prevent the formation of the typical Fe–S apical bonds in dimerised bisdithiolene complexes as observed in **2**.

As expected for well isolated paramagnetic species the magnetic susceptibility measurements[¶] indicate for **1** a large effective magnetic moment, μ_{eff} , of 2.34 μ_{B} per Fe atom, almost constant from room temperature down to circa 25 K (Fig. 4). Below this temperature there is a noticeable decrease in μ_{eff} due to predominant antiferromagnetic interactions, most likely mediated by hydrogen bonds between the N atoms of the ligands. This value of μ_{eff} above 30 K corresponds to a $S = 1/2$ spin state with $g = 2.7$, demonstrating that this complex presents a low spin configuration. In this respect it is worth remembering that both high spin⁸ and low spin configurations⁹ have been reported in dimerised Fe^{III} complexes with other bis dithiolate ligands.

The measurement of the magnetic properties of **2** denotes the presence of variable and difficult to control amounts of paramagnetic impurities which hamper a quantitative analysis of the data. However the results are qualitatively consistent with a singlet ground state as observed in other dimerised Fe(III) complexes.^{8,9}

This observation of an undimerised Fe^{III} complex was, from previous literature data, totally unexpected. The fact that there is dimerisation of the same $[\text{Fe}(\text{qdt})_2]^-$ complex with another cation as found in **2**, clearly demonstrates that the occurrence of a square planar coordination or a dimeric structure in Fe^{III} complexes critically depends on the crystal environment created by the counter cation, and in this case the $\text{Fe}\cdots\text{H}$, $\text{Fe}\cdots\text{C}$ and $\text{S}\cdots\text{H}$ interactions. A more clear and detailed demonstration of such an effect is expected to be given by a systematic study of salts of this

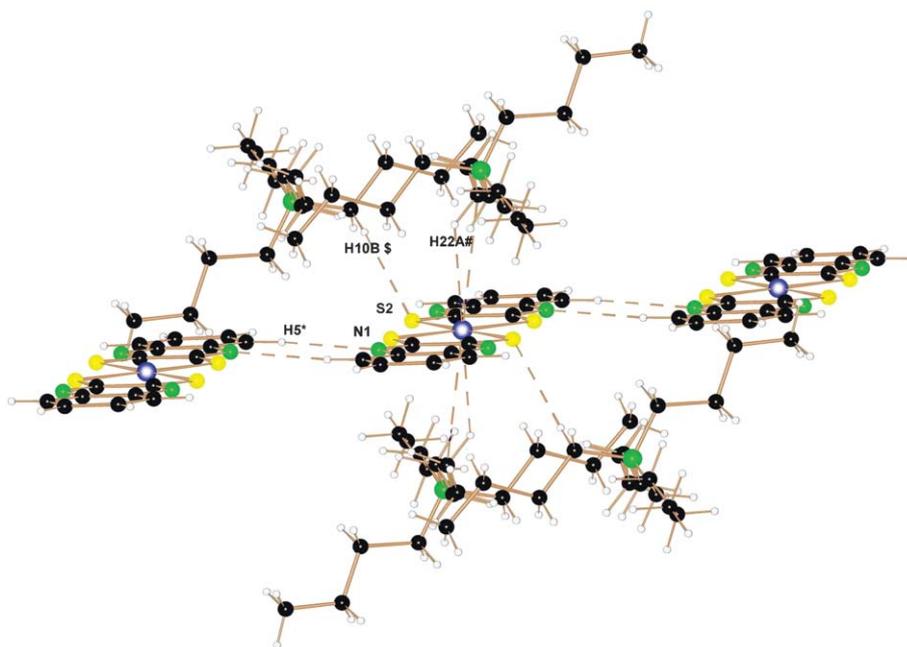


Fig. 2 Partial view of the crystal structure of **1**. Two pairs of hydrogen contacts, $\text{N1}\cdots\text{H5}^*$ at 2.66 Å connect the complexes into two chains along $a + b$ and $a - b$. Short apical contacts, $\text{Fe}\cdots\text{H22A}^\#$ at 2.95 Å and $\text{Fe}\cdots\text{C22}^\#$ at 3.670(8) Å connect the metal bisdithiolate to H atoms from cations placed above and below the complex. Short contact $\text{S2}\cdots\text{H10B}^s$ at 2.86 Å. Atoms marked with (*), (#) and (s) are at symmetry positions $(3/2 - x, 1/2 - y, 1 - z)$, $(1 - x, y, 1/2 - z)$ and $(x, y - 1, z)$ respectively.

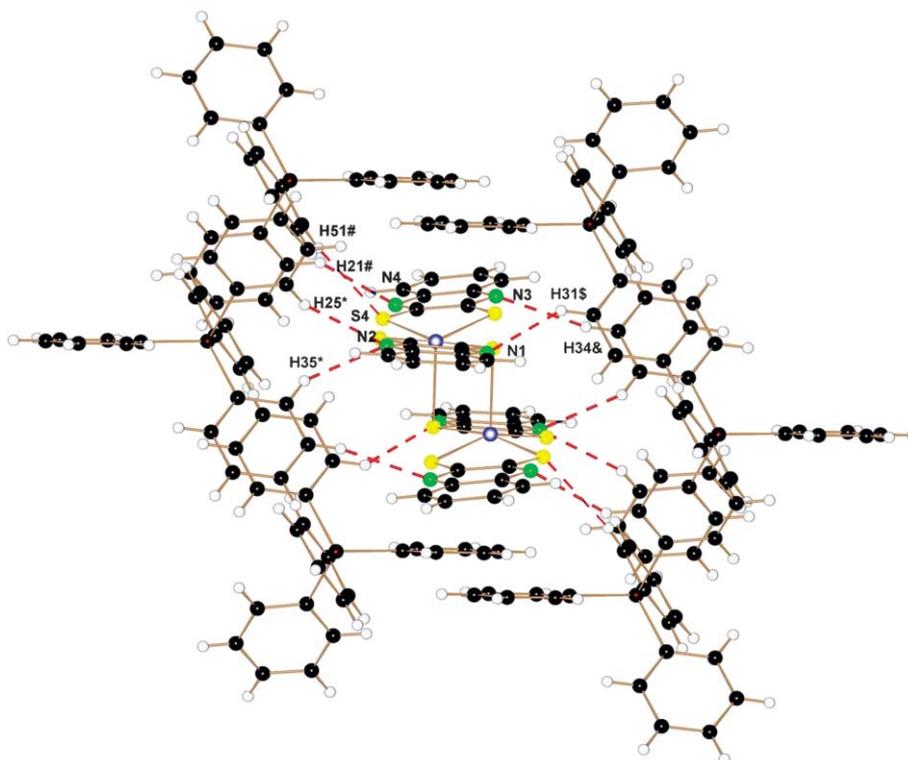


Fig. 3 Partial view of the crystal structure of **2** showing dimerised $[\text{Fe}(\text{qdt})_2]^-$ anions connected to cations (only 6 are shown) by hydrogen bonds and contacts. The C–H \cdots N bonds depicted have H \cdots N separations ranging from 2.44 Å to 2.67 Å. Atoms marked with (*), (#), (\$) and (&) are at symmetry positions (x, y, z) , $(2 - x, 1 - y, 1 - z)$, $(x, y - 1, -z)$ and $(1 - x, -y, 1 - z)$ respectively.

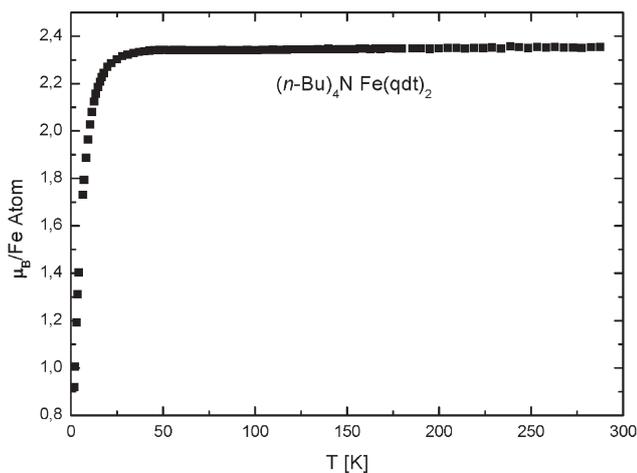


Fig. 4 Effective magnetic moment, μ_B , of **1** as a function of temperature, T .

complex with different anions, presently under way in our laboratory.

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Notes and references

‡ General procedure: 0.8 g of metallic sodium was dissolved in 50 mL of methanol p.a. To this solution 2.0 g (0.01 mol) of 2,3-quinoxalinedithiol was added and stirred at room temperature, followed by dropwise addition, over a period of 15 min, of a solution of 0.84 g (0.005 mol) of FeCl_3 in

methanol p.a. The final solution was filtered and a solution of 1.9 g (0.005 mol) of *n*-Bu $_4$ Ni [or 2.2 g (0.005 mol) of Ph $_4$ AsBr] in methanol was added to the filtrate. Water was added slowly until the start of incipient crystallization and then the mixture was left overnight. The dark crystalline precipitate was collected by filtration and recrystallised by dissolution in a minimum amount of methanol with a few drops of ammonia, followed by addition of water until the start of incipient crystallisation. The solution was left at 5 °C overnight and the Fe complexes were collected as shining black crystals by filtration. Suitable crystals for X-ray diffraction were obtained by slow evaporation of a concentrated solution in MeOH (in the case of **1**) or CH $_3$ CN (in the case of **2**) with a few drops of ammonia.

(*n*-Bu) $_4$ N[Fe(qdt) $_2$] (**1**), 45% yield, mp 123–124 °C. Anal. Calc. for C $_{32}$ H $_{44}$ N $_5$ S $_4$ Fe (682.81): N, 10.26; C, 56.29; H, 6.49; S, 18.78%. Found: N, 10.00; C, 56.86; H, 6.80; S, 18.53%. IR(KBr pellet) cm $^{-1}$: 3060 (w, Ar–H), 2960–2870 (m, C–H), 1465 (s, C=N), 330 (m, S–Fe).

(Ph) $_4$ As[Fe(qdt) $_2$] (**2**), 38% yield, mp 160–161 °C. Anal. Calc. for C $_{40}$ H $_{28}$ N $_4$ S $_4$ FeAs (823.73): N, 6.80; C, 58.32; H, 3.43; S, 15.57%. Found: N, 6.01; C, 58.66; H, 4.60; S, 14.40%. IR(KBr pellet) cm $^{-1}$: 3065 (w, Ar–H), 1438 (s, C=N), 360 (m, S–Fe).

§ Crystal data for **1**: C $_{32}$ H $_{44}$ N $_5$ S $_4$ Fe, $M = 682.81$, monoclinic, $C2/c$, $a = 22.290(3)$ Å, $b = 8.5089(9)$ Å, $c = 19.112(2)$ Å, $\beta = 107.798(12)^\circ$, $V = 3451.4(7)$ Å 3 , $Z = 4$, $D_c = 1.314$ Mg m $^{-3}$, $\mu = 0.708$ mm $^{-1}$ (Mo–K α $\lambda = 0.71069$ Å), $T = 293(2)$ K, reflections measured 3425, unique data 2916 ($R_{\text{int}} = 0.0597$) which were used in all calculations. Final R indices $R1 = 0.0503$, $wR2$ on $F^2 = 0.1169$ [$I > 2\sigma(I)$], goodness-of-fit 0.962.

Crystal data for **2**: C $_{40}$ H $_{28}$ As $_2$ Fe $_2$ N $_8$ S $_8$, $M = 1647.43$, triclinic, $P\bar{1}$, $a = 10.6406(12)$ Å, $b = 11.3943(10)$ Å, $c = 15.4041(19)$ Å, $\alpha = 100.228(9)^\circ$, $\beta = 91.538(8)^\circ$, $\gamma = 100.917(8)^\circ$, $V = 1801.1(3)$ Å 3 , $Z = 1$, $D_c = 1.519$ Mg m $^{-3}$, $\mu = 1.598$ mm $^{-1}$ (Mo–K α $\lambda = 0.71069$ Å), $T = 295(2)$ K, reflections measured 7330, unique data 7053 ($R_{\text{int}} = 0.0411$) which were used in all calculations. Final R indices $R1 = 0.0537$, $wR2$ on $F^2 = 0.0821$ [$I > 2\sigma(I)$], goodness-of-fit 0.949.

CCDC reference numbers 262344 and 298265. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602268e

¶ Static susceptibility was measured in the range 4–300 K by the longitudinal Faraday technique under a magnetic field of 5 T with a gradient of 1 T m $^{-1}$, and the paramagnetism calculated assuming a

diamagnetic contribution of **1** estimated as $-4.106 \times 10^{-4} \text{ emu mol}^{-1}$, from tabulated Pascal constants ($1 \text{ emu mol}^{-1} = 4\pi \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$).

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