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The Crystal Structure of Bis-(3,5-diphenyl-1,2-dithiolium) Tetrachloroferrate(III) Chloride

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The crystal structure has been determined from three-dimensional X-ray diffractometer data. Crystals are tetragonal, space group $P4/ncc$ (D_{4h}^{4}, No. 126) with $a=b=12{\cdot}91$, $c=19{\cdot}80$ Å and $Z=4$. Crystals are composed of discrete SbzSbz$^+$, Cl$^-$ and [FeCl$_4$]$^-$ ions occupying sites of symmetry C_2, D_{2h} and C_4 respectively. Though not required by space-group symmetry, one chlorine atom of the [FeCl$_4$]$^-$ ion lies on the crystallographic C_4 axis, the three remaining chlorines being rotationally disordered. No short [FeCl$_4$]···SbzSbz contacts, such as occur in the tetrachloroferrate(II) salts, are observed; the chloride ions at the D_{2h} sites are each involved in four equivalent Cl···S contacts of length 3·18 Å, some 0·47 Å shorter than the sum of the van der Waals radii.

Introduction

Tetrachlorometallate(II) salts of the 3,5-diphenyl-1,2-dithiolium cation [SbzSbz$^+$, Fig. 1] exhibit structural polymorphism. Various polymorphs which have been isolated, and in some cases completely characterized by single-crystal X-ray diffraction studies, are listed in Table 1 (Rusholme, 1970). The list is probably not exhaustive.

Two crystalline products are also obtained, though sequentially, from the procedure used to prepare the tetrachloroferrate(II) salt characteristic of the α isomer of Table 1. The preparative procedure, common to all of the salts of Table 1, involves treatment of a 1% solution of dibenzoylmethane in ethanol (at −10°C), first with hydrogen sulphide gas for *ca.* thirty minutes, then with hydrogen chloride gas until the solution changes colour, followed by addition either of the appropriate metal(II) chloride, a metal(III) complex, or the metal itself. Dark-green prismatic crystals of the tetrachloroferrate(II) salt usually separate out from the reaction mixture in less than a day. However, on prolonged standing (>2 weeks) of the filtrate, pale-yellow tetragonal prismatic crystals were slowly deposited.

Table 1. *Structural isomerism of* (SbzSbz)$_2$[MCl$_4$] *salts*

Metal M	Structural types	
Mn	α	γ
Fe	α	
Co	γ	
Zn	α	γ
Cd	α	
Hg	α	β

Table 1 (*cont.*)

Structural types		Space group	*a*	*b*	*c*	α	β	γ
α	(Fe)	$C\bar{1}$	16·22 Å	22·28 Å	16·95 Å	95°57′	82°44′	100°21′
β	(Hg)	$C2/c$ or Cc	14·91	11·51	20·15		118°46′	
γ	(Zn)	$P2_1/n$	10·30	16·62	17·89		98°20′	

Diffuse reflectance spectra of the two species show (Rusholme, 1970) marked differences in the region *ca.* 500–1800 nm (Fig. 2) and, in turn, the spectrum of the green tetrachloroferrate(II) salt differs appreciably (in the same region) from the spectra of the remaining (SbzSbz)$_2$[MCl$_4$] salts of Table 1. Somewhat analogous differences between the visible spectra of these salts, and that of the 3,5-dimethyl-1,2-dithiolium salt of [FeCl$_4$]$^{2-}$, *viz.* (SacSac)$_2$[FeCl$_4$], which has its origin in interionic charge transfer (Mason, McKenzie, Robertson & Rusholme, 1968; Freeman, Milburn, Nockolds, Hemmerich & Knauer, 1969), prompted us to undertake single-crystal X-ray analyses of both the green and yellow materials. In view of the degree of polymorphism exhibited by the tetrachlorometallate(II) SbzSbz salts, it was assumed, incorrectly, that both materials (green and yellow) were simply structural isomers of (SbzSbz)$_2$[FeCl$_4$]. In the case of the dark-green material, this formulation has subsequently been confirmed (Rusholme, 1970). However, reconsideration of the spectral data, together with results of the present single-crystal X-ray diffraction study, indicates conclusively that the correct formulation for the yellow material is bis-(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate(III) chloride.

Experimental

Crystals of bis-(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate(III) chloride [(SbzSbz)$_2$(FeCl$_4$)Cl;

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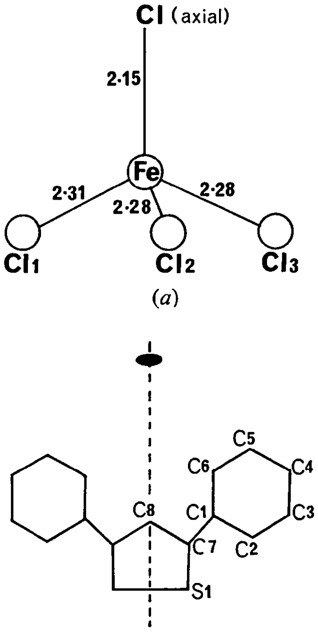
$C_{30}H_{22}S_4Cl_5Fe$], obtained by the procedure outlined above, occur as uniaxial pale-yellow tetragonal prisms generally elongated along the direction of the optic axis.



(a)

(b)

Fig. 1. $(SbzSbz)_2[FeCl_4]Cl$. (a) Atom nomenclature and M–Cl bond lengths. (b) Atom nomenclature in the dithiolium cation.

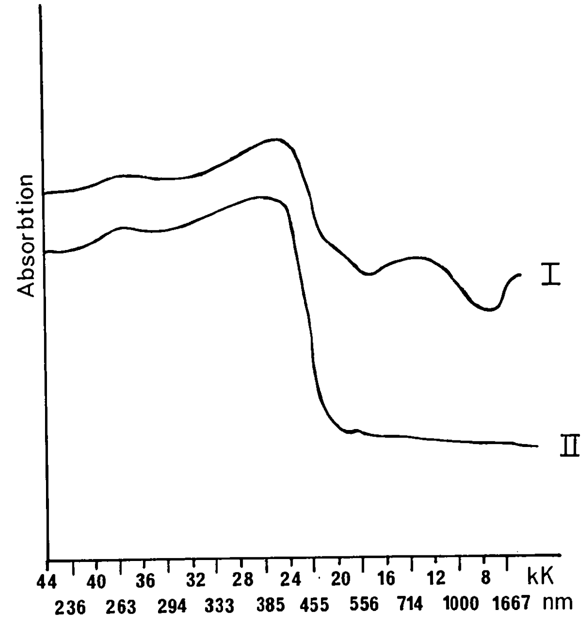


Fig. 2. $(SbzSbz)_2[FeCl_4]Cl$ and $(SbzSbz)_2[FeCl_4]$: diffuse reflectance spectra. I: Bis-(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate(II). II: Bis-(3,5-diphenyl-1,2-dithiolium) tetrachloroferrate(III) chloride.

Crystal data

Found: C, 48·7; H, 3·1; S, 17·2; Cl, 23·7; residue, 7·3 %. Analysis calculated for $C_{30}H_{22}S_4Cl_5Fe$: C, 48·4; H, 3·0; S, 17·2; Cl, 23·8; Fe, 7·5 %. Diffraction symmetry D_{4h} ($4/mmm$). Tetragonal, $a=b=12·91$ (1), $c=19·80(1)$ Å, $V_c=3300$ Å^3 (from high-angle data on precession photographs, Zr-filtered Mo $K\alpha$ radiation, $\lambda=0·7107$ Å, $\mu=7·6$ cm^{-1}). Systematic absences: $hk0, h+k=2n+1$; $0kl$, $l=2n+1$; hhl, $l=2n+1$; space group $P4/ncc$ (D_{4h}^4, No. 126); $\varrho_{\text{obs}}=1·48$ (1) g cm^{-3} (flotation, benzene/ tetrabromoethane); $\varrho_{\text{calc}}=1·496$ g cm^{-3}. $M=743·92$; $Z=4$; $F(000)=1508$.

Data collection

Reflexion intensities were measured on a Hilger and Watts four-circle diffractometer using Mo $K\bar{\alpha}$ radiation with 95 % discriminator pass. The specimen crystal was oriented with its optic axis (c) approximately coincident with the instrumental φ axis. Cell dimensions and accurate orientation-matrix parameters were derived in the usual way by least-squares analysis of 2θ, ω, χ and φ values for 12 high-angle reflexions (Busing & Levy, 1967). Intensity data were recorded using a θ–2θ scan mode and balanced (Y/Zr) filters. The scan velocity (1° min^{-1}, 2θ) and scan range (1·8°, 2θ) were held constant for all reflexions. Backgrounds were measured in stationary-crystal stationary-counter mode, at each extreme of the scan range (*i.e.* $2\theta\pm0·9°$), for a total time of 2×18 s. All reflexions of form $(+)hkl$ (one octant) within the range $3°\le2\theta\le40°$ were recorded. Intensities of three standard reflexions were monitored every 50 unique reflexions. No significant variation of the intensities of the standards was observed during the entire run. Dimensions of the specimen crystal (cubic) were $0·25\times0·25\times0·25$ mm parallel to **a**, **b** and **c** respectively.

Data were subject to the acceptance criteria $I/\sigma(I)\ge3·0$ and $\Delta B/\sigma(B)\le3·0$. Data were also accepted if $\Delta B/\sigma(B)>3·0$ and $I/\sigma(I)\ge5·0$, but with $(\delta B1+\delta B2)$ in the formula for I replaced by $2\delta_{\min}^B$, where $\delta B_{\min}$ is the smaller of the modulii of $\delta B1$ and $\delta B2$, and the symbols have the meaning defined in the preceding paper (Mason *et al.*, 1974). Data were subsequently corrected for Lorentz and polarization effects but no correction was applied for specimen absorption ($\mu=7·6$ cm^{-1}). The terminal data set contained 740 unique [D_{4h}^4] reflexions. The stochastic R value (R_s) for the data set was 0·023.

Solution and refinement

Initially, as a matter of computational convenience, reflexion forms were averaged only under the symmetry equivalences of the orthorhombic Laue group $D_{2h}(mmm)$ and Patterson, Fourier and least-squares calculations were carried out in the appropriate orthorhombic sub-groups ($Pmmm$ and $Pccn$) of $P4/mmm$ and $P4/ncc$ respectively. The statistical discrepancy index (R_s) for this experimental 'orthorhombic' data set was 0·033. Solution was sought initially in terms of a structure comprising two dithiolium cations, one tetrachloroferrate(II) anion and *ca.* 27 mass units of included solvent.* For $Z=4$ (in $P4/ncc$) the anion is required to occupy a site of symmetry 4, $\bar{4}$ or 222, and the cations to occupy equivalent sites each of symmetry 2. In the absence of rotational disordering, site symmetry 4 is not permissible for the anion. Nevertheless, both conventional and sharpened (Jacobson, Wunderlich & Lipscomb, 1961) Patterson syntheses could only be interpreted satisfactorily in terms of a structure involving site symmetry 4 for the metal atom and, in addition, occupancy of the 222 site by an atom of scattering power roughly equivalent to chlorine or sulphur. For initial phasing purposes, chlorine scattering factors were assumed for the atom at the 222 site. The implied alteration in structural formulation, either to $(\mathrm{SbzSbz})_2(\mathrm{Fe^{II}Cl_4}).\mathrm{HCl}$ or to $(\mathrm{SbzSbz})_2(\mathrm{Fe^{III}Cl_4})\mathrm{Cl}$, at once resulted in better agreement for the analytical data and also accounted, more or less satisfactorily, for the 27 mass unit discrepancy deriving from comparison of observed and calculated crystal densities (see above). For the initial scattering model, contributions were included only from iron, sulphur and the chlorine in the 222 special position. A Fourier synthesis, phased from this model, allowed the location of all carbon atoms of the 3,5-diphenyl-1,2-dithiolium cations and confirmed the absence of any coordination sphere around the atoms at the 222 sites. Around the metal atom the situation was less clear, the electron-density distribution apparently indicating square-pyramidal coordination (maximum densities *ca.* 3 and 7 e Å^{-3} for basal and axial ligands respectively), strictly analogous to that inferred directly from the Patterson maps. Inclusion of carbon-atom contributions (with the 222 atom reformulated as $\mathrm{Cl^-}$) followed by block-diagonal least-squares refinement of those parameters describing the still incomplete scattering model gave a discrepancy index $[R=\sum||F_o|-|F_c||/\sum|F_o|]$ of 0·25. A subsequent Fourier synthesis again indicated a square-pyramidal peak distribution about the metal atom, consistent with rotational disordering of an approximately tetrahedral $[\mathrm{FeCl_4}]^{n-}$ ion about the C_4 axis directed through the metal and axial halogen atoms. 12 atoms of one quarter the scattering power of chlorine were then fitted to the 'basal' electron distribution indicated in the Fourier map. This model implies some distortion from a regular tetrahedral arrangement with, notably, two (basal) angles less than, and one angle greater than the tetrahedral value (Table 4). Coordinates of these chlorine atoms, with fixed fractional site occupancy, were not subsequently varied. With carbon atoms and the basal chlorine atoms restricted to isotropic thermal parameter refinement, convergence was achieved at $R_1=0·10$. Reflexion forms equivalent under Laue group D_{4h} ($4/mmm$) were then averaged to yield the unique tetragonal data set. The scattering model was extended to include contributions from hydrogen atoms of the $\mathrm{SbzSbz^+}$ cations. Neither the calculated hydrogen coordinates (C–H = 1·07 Å assumed) nor the assigned thermal parameters ($B_\mathrm{H}=6·5$ Å^2 assumed) were varied in subsequent refinement cycles. With all non-hydrogen atoms anisotropic (except the basal chlorines), subsequent block-diagonal least-squares analysis converged to $R=0·083$.

Calculated parameter shifts for the terminal refinement cycles were uniformly less than one fifth of the e.s.d. in the corresponding parameter. The terminal difference Fourier map exhibits electron-density excursions of *ca.* ±2 e Å^{-3} in the regions of the basal chlorines; the distribution of these excursions suggests, not unexpectedly, that agreement might be improved by use of a hindered-rotor model.

Structural data are summarized in Tables 2, 3 and 4.* Atom scattering factors for C, Fe, S, Cl and $\mathrm{Cl^-}$ were taken from *International Tables for X-ray Crystallography* (1962). For hydrogen atoms the values of Stewart, Davidson & Simpson (1965) were used. The function minimized during the least-squares analyses was $\sum w||F_o|-|F_c||^2$ with $w=1$ for all reflexions. Parameter standard errors, given throughout in parentheses, derive in the usual way from inversion of the block-diagonal least-squares matrix.

Table 2. $(\mathrm{SbzSbz})_2[\mathrm{FeCl_4}]\mathrm{Cl}$: *atomic coordinates and isotropic thermal parameters*

Atom nomenclature is as defined in Fig. 1. Parameters quoted without standard errors were not refined. An asterisk indicates a parameter fixed by space-group symmetry.

	x/a	*y/b*	*z/c*	*B*(Å^2)
Fe	0·2500 (*)	0·2500 (*)	0·1962 (1)	
S(1)	0·4340 (3)	0·8958 (3)	−0·2980 (2)	
Cl (ion)	0·7500 (*)	0·2500 (*)	0·2500 (*)	
Cl (axial)	0·2500 (*)	0·2500 (*)	0·3047 (3)	
C(1)	0·4935 (9)	0·4164 (9)	0·3720 (6)	
C(2)	0·4171 (10)	0·4213 (11)	0·4196 (7)	
C(3)	0·4283 (13)	0·3736 (11)	0·4820 (7)	
C(4)	0·5171 (11)	0·3194 (10)	0·4947 (7)	
C(5)	0·5936 (10)	0·3116 (10)	0·4479 (7)	
C(6)	0·5833 (10)	0·3609 (10)	0·3863 (6)	
C(7)	0·4860 (8)	0·4700 (8)	0·3062 (6)	
C(8)	0·5471 (9)	0·4529 (9)	0·2500 (*)	
Cl(1)	0·2549	0·0780	0·1637	7·0
Cl(2)	0·0967	0·1900	0·1544	12·0
Cl(3)	0·4033	0·1900	0·1544	12·0
H(1)	0·3466	0·4621	0·4085	6·5
H(2)	0·3676	0·3762	0·5197	6·5
H(3)	0·5292	0·2849	0·5436	6·5
H(4)	0·6620	0·2644	0·4592	6·5
H(5)	0·6452	0·3583	0·3494	6·5
H(6)	0·6060	0·3944	0·2500 (*)	6·5

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* To account for the difference between the observed crystal density [1·48 (1) g cm^{-3}] and that calculated for four (SbzSbz) [FeCl$_4$] structural units only per cell.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30275 (2 pp.). Copies can be obtained through The Executive Secretary, IUCr, 13 White Friars, Chester CH1 1NZ, England.

Table 3. $(SbzSbz)_2[FeCl_4]Cl$: *anisotropic thermal parameters*

$T=[\exp\ -(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+kl\beta_{23}+hl\beta_{13}+hk\beta_{12})]$.

An asterisk indicates a parameter fixed by space-group symmetry.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Fe	0·01074 (4)	0·01074 (4)	0·00220 (1)	0·00000 (*)	0·00000 (*)	0·00000 (*)
S(1)	0·00754 (4)	0·00723 (4)	0·00342 (2)	−0·00194 (5)	0·00137 (5)	−0·00578 (6)
Cl (ion)	0·00489 (4)	0·00489 (4)	0·00385 (2)	0·00000 (*)	0·00000 (*)	−0·00031 (8)
Cl (axial)	0·0210 (1)	0·0210 (1)	0·00235 (2)	0·00000 (*)	0·00000 (*)	0·00000 (*)
C(1)	0·0061 (1)	0·0064 (1)	0·00298 (6)	0·0013 (2)	−0·0003 (2)	0·0006 (2)
C(2)	0·0088 (2)	0·0111 (2)	0·00347 (7)	0·0014 (2)	0·0017 (2)	0·0076 (3)
C(3)	0·0138 (2)	0·0107 (2)	0·00311 (7)	0·0010 (2)	0·0032 (2)	0·0070 (4)
C(4)	0·0104 (2)	0·0084 (2)	0·00283 (6)	0·0002 (2)	−0·0017 (2)	0·0011 (3)
C(5)	0·0081 (2)	0·0094 (2)	0·00360 (7)	0·0009 (2)	−0·0034 (2)	−0·0004 (3)
C(6)	0·0082 (2)	0·0087 (2)	0·00325 (7)	0·0002 (2)	−0·0022 (2)	0·0012 (3)
C(7)	0·0049 (1)	0·0058 (1)	0·00311 (6)	−0·0012 (2)	−0·0007 (2)	0·0028 (2)
C(8)	0·0067 (1)	0·0068 (1)	0·00349 (6)	−0·0018 (2)	−0·0018 (2)	0·0046 (2)

Table 4. $(SbzSbz)_2[FeCl_4]Cl$: *bond lengths and angles*

Fe—Cl (axial)	2·15 (1) Å	C(3)-C(4)	1·37 (2) Å
Fe—Cl(1)	2·31	C(4)-C(5)	1·36 (2)
Fe—Cl(2)	2·28	C(5)-C(6)	1·38 (2)
Fe—Cl(3)	2·28	C(6)-C(1)	1·39 (2)
S(1)-S(1′)	2·023 (5)	C(7)-C(1)	1·48 (2)
S(1)-C(7)	1·71 (1)	C(7)-C(8)	1·38 (1)
C(1)-C(2)	1·37 (2)	Mean C-H	1·08
C(2)-C(3)	1·39 (2)	S···Cl (ion)	3·176 (4)

Cl—Fe—Cl (axial)	106°	C(3)-C(4)-C(5)	121 (1)°
Cl(2)-Fe—Cl (axial)	111	C(4)-C(5)-C(6)	120 (1)
Cl(3)-Fe—Cl (axial)	111	C(5)-C(6)-C(1)	120 (1)
Cl(1)-Fe—Cl(2)	102	C(6)-C(1)-C(2)	119 (1)
Cl(1)-Fe—Cl(3)	104	C(6)-C(1)-C(7)	118 (1)
Cl(2)-Fe—Cl(3)	120	C(2)-C(1)-C(7)	123 (1)
		C(1)-C(7)-C(8)	127 (1)
S(1′)-S(1)-C(7)	95·8 (4)	C(1)-C(7)-S(1)	118 (1)
C(1)-C(2)-C(3)	121 (1)	C(8)-C(7)-S(1)	115 (1)
C(2)-C(3)-C(4)	119 (1)	C(7)-C(8)-C(7′)	118 (1)

Discussion

Despite the lack of precise dimensions, there is little doubt that the anion is $[FeCl_4]^-$ rather than $[FeCl_4]^{2-}$. The axial Cl–Fe distance, which appears reasonably well defined by the diffraction data, is 2·15 (1) Å. Allowing for some shortening due to librational effects, this value is in reasonable agreement with that (*ca.* 2·19 Å) characteristic of the tetrachloroferrate(III) anion (Trinh-Toan & Dahl, 1971). In contrast, the characteristic Fe–Cl distance in $[FeCl_4]^{2-}$ is *ca.* 2·31 Å (Freeman *et al.*, 1974; Mason *et al.*, 1974; Trinh-Toan & Dahl, 1971). More direct evidence for the $[FeCl_4]^-$ formulation is provided by the diffuse reflectance spectra of Fig. 2. In particular, the spectrum of the present complex (curve II) lacks any absorption in the region 1250–2000 nm. Absorption in this range is characteristic of the $[FeCl_4]^{2-}$ anion (*cf.* the spectrum of the fully characterized complex $[SbzSbz^+]_2[FeCl_4]^{2-}$: curve I) and has been assigned to the $^5E \leftarrow {}^5T_2$ transition (Burbridge & Goodgame, 1968; Gill, 1961; Heath, Martin & Stewart, 1969 *a*, *b*; Quagliano, Banerjee, Goedken & Vallarino, 1970). The *d–d* spectrum of $[FeCl_4]^-$ has also been reported (Balt, 1967; Gill, 1961; Kistenmacher & Stucky, 1968); the transitions, being spin-forbidden, have very low extinction coefficients. It is possible, however, that the most intense transition found by Kistenmacher & Stucky (1968) for single crystals of tetrachlorophosphonium tetrachloroferrate(III) ($\varepsilon=1·8$ mol^{-1} l cm^{-1}, 536 nm, $^6A_1 \leftarrow {}^4T_2$) is just resolved in the spectrum of $[SbzSbz^+]_2[FeCl_4]Cl$ at 543 nm. The ultraviolet spectrum of $[FeCl_4]^-$ has also been discussed (Bird & Day, 1968) but in the present complex this region is dominated by the intense cation absorption.

The $[FeCl_4]^-$ ions are each located in a highly symmetrical environment, *viz.* a large square-pyramidal cavity within the lattice, the four equivalent triangular faces being defined by four equivalent dithiolium cations. The packing arrangement, with one 'threefold' axis of the (essentially) tetrahedral ion coincident with the (crystallographic) C_4 axis of the cavity, would appear to provide a reasonably effective match between ion and site geometry. Within such an environment it might be expected that (*a*) there would be only small energy differences between any given orientation of the basal chlorine atoms and (*b*) there would be little restraint on relatively large rocking or librational modes about directions other than the C_4 axis. The presence of both effects is indicated.

Unlike the situation in $[FeCl_4]^{2-}$ dithiolium complexes (Freeman *et al.*, 1974; Mason *et al.*, 1974), there are no close contacts between the tetrachloroferrate and dithiolium ions. However, the chloride ions located at the 222 symmetry sites each make four equivalent Cl···S contacts of 3·176 (3) Å, compared with the van der Waals radii sum of 3·65 Å (Pauling, 1960). These contacts are comparable in distance to the Cl···S contacts between the counter ions in $(SacSac)_2[FeCl_4]$ (Freeman *et al.*, 1974) and $(SbzSbz)_2[FeCl_4]^-$ (Mason *et al.*, 1974) but are slightly shorter than the inter-ion contacts found by Hordvik & Kjøge (1965), Hordvik (1965), Hordvik & Joys (1965) and Hordvik & Sletten (1966 *a*, *b*) for various dithiolium halides.

The 3,5-diphenyl-1,2-dithiolium cations have exact (crystallographic) C_2 symmetry, the five-membered ring being planar to within experimental error. Except for small differences in dihedral angle between the fiveand six-membered rings, the dimensions of the cation are virtually identical with those found in its $[MCl_4]^{2-}$ salts ($M = Fe, Hg$) (Rusholme, 1970). As with other 1,2-dithiolium cations, bond lengths and bond angles are indicative of substantial cyclic delocalization in the five-membered ring system.

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The Crystal Structures of 2,2′-Bipyridine.2ICl and 2,2′-Bipyridine.2IBr

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The crystal structures of 2,2′-bipyridine.2ICl and 2,2′-bipyridine.2IBr have been determined from three-dimensional diffractometer data to give $R = 2{\cdot}9\%$ and $4{\cdot}0\%$ respectively. 2,2′-Bipyridine.2ICl crystallizes in $P2_1/n$ with $a = 11{\cdot}833$ (7), $b = 12{\cdot}427$ (7), $c = 10{\cdot}163$ (5) Å, and $\beta = 101{\cdot}76$ (3)°; $Z = 4$. 2,2′-Bipyridine.2IBr crystallizes in $Pnna$, with $a = 12{\cdot}971$ (4), $b = 11{\cdot}163$ (4), $c = 10{\cdot}387$ (4) Å; $Z = 4$. In the chlorine compound the dihedral angle between the pyridine rings is 88·6°, in the bromine compound 52·9°. A short intramolecular approach of the two iodine atoms in the IBr adduct (4·09 Å) is observed.

Introduction

Several significant differences in the chemical structure of 2,2′-bipyridine.2ICl and 2,2′-bipyridine.2IBr (hereinafter referred to as bipy.2ICl and bipy.2IBr) were inferred from a recent Mössbauer spectroscopic study of ^{129}I (Wynter, Hill, Bledsoe, Shenoy & Ruby, 1969). For example, bipy.2ICl has more π bonding than the IBr adduct. Furthermore, from the larger asymmetry parameter of bipy.2IBr, the authors suggested that bipy.2ICl exists in a *trans* conformation in the solid state, but bipy.2IBr crystallizes in a *cis* conformation. Previously, it had been found that uncomplexed 2,2′-bipyridine crystallizes as a planar molecule with the two nitrogen atoms *trans* to one another (Merritt & Schroeder, 1956). Structural studies have also been done on the ICl and IBr adducts to pyridine (Hassel & Rømming, 1956; Dahl, Hassel & Sky, 1967) showing the N–I–X bonding to be linear. This study was undertaken to compare the detailed geometry of bipy.2ICl, $C_{10}H_8N_2$.2ICl, and bipy.2IBr, $C_{10}H_8N_2$.2IBr.

Experimental

Sample preparation

Both the ICl and IBr adducts are prepared as fine powders by slowly mixing dilute CCl_4 solutions of 2,2′-bipyridine and ICl or IBr (Popov & Pflaum, 1957; Yagi, Popov & Person, 1967). Crystals of both compounds can be grown by sublimation on to a cold