X-ray crystal and molecular structure of dichlorobis [2(1H)-pyridinethione-S]iron(II)

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Attempts to prepare the mixed ligand complex, $FeCl_2(pyS)(Ph_3P)_2$ from the reaction of iron(III) chloride with 2(1H)-pyridinethione-S(HpyS) and triphenylphosphine(Ph_3P) in ethanol instead formed $FeCl_2(HPyS)_2$ characterized by X-ray crystallography. The structure was determined by the heavy atom method, using Mo $K\alpha$ diffractometer data, and refined by full-matrix least squares to R = 0.049 for 1123 observed reflections. The molecule possesses twofold symmetry with a distorted tetrahedral geometry about the iron(II) center with S-Fe-S and Cl-Fe-Cl bond angles of 98.76(5)° and 115.79(5)° and Fe-S and Fe-Cl bond distances 2.345(1) Å and 2.288(1) Å, respectively. Hydrogen bonding between NH and chlorine atoms leads to a polymeric type structure of linked molecules running approximately parallel to the *a* axis.

Introduction

In the recent past there has been a considerable interest in the coordination properties of 2-mercaptopyridine [hereafter HpyS, (1 and (2)] containing the -N(H)-C(=S)-chromophore which is a useful model for sulphur containing analogues of purine and pyrimidine bases (Mura et al., 1985; Raper, 1985). Generally, HpyS coordinates via the S atom (Lobana and Bhatia, 1990; Raper, 1985), although various other modes such as S,N-chelating (Deeming et al., 1986), S,N-bridging (Deeming et al., 1986: Kinoshita et al., 1983) and S unidentate with a weak M \cdots N interaction (Castineiras et al., 1986) are also known.



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Only a few Fe(II) or Fe(III) complexes of (1) or (2), namely, FeX₂(HpyS)₂ (X = Cl, Br) (Evans and Wilkinson, 1974), Fe(NO)₂(pyS)₂(H₂O) (Jezierski and Jezowska-Trazeloiatowska, 1984), (Et₄N)[Fe(pyS)₃] (Rosenfield *et al.*, 1986) and (C₅H₄N)(CO)₆—Fe₂— (μ_4 —S)—Fe₂(CO)₆(pyS) (Bargue and Grandjean, 1975) have been reported. X-Ray structures for the last two complexes have been determined. In continuation of our interest in preparing the mixed ligand complexes (Lobana *et al.*, 1989), using pyridinethiols and tertiaryphosphines, the present work was undertaken. However, instead of forming a mixed ligand complex FeCl₂(pyS)(Ph₃P)₂ from the reaction of FeCl₃ with HpyS and Ph₃P, an iron(II) complex, FeCl₂(HpyS)₂ was formed whose X-ray crystal structure is reported herein.

Experimental

To a solution of iron(III) chloride (0.146 g) in ethanol (25 cm³) was added solutions of HpyS (0.1 g) in ethanol (15 cm³) and Ph₃P (0.203 g) in chloroform (15 cm³). The mixture was refluxed for 2 hr and concentrated to one third of its original volume. Slow evaporation gave yellow platey crystals.

A crystal of dimensions 0.4, 0.5, 0.1 mm was

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Table 1. Crystal data					
Molecular formula	$C_{10}H_{10}Cl_2FeN_2S_2$				
M_r	349.08				
Crystal system	Monoclinic				
Space group	C_c^2				
a	9.394(4) Å				
b	11.418(6)				
с	13.649(2)				
β	109.17(2)*				
V _c	1382(2) Å ³				
Z	4				
D_c	1.677 g cm^{-3}				
F(000)	704				
$\mu(Mo K\alpha)$	17.5 cm ⁻¹				

examined on an Enraf Nonius CAD4 diffractometer, using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). An accurate unit cell was obtained by a least-squares fit of 25 reflections [(sin θ)/ λ in the range 0.37-0.31]. An ω -2 θ scan (minimum scan speed 3.3°/min to a maximum collection time of 90 s) was used to collect the intensity data which were corrected for Lorentz and polarization and an empirical absorption correction (ψ -scan) was applied. A reference reflection monitored every 1 hr of exposed X-ray time showed a 3% decrease during the period of data collection (43 h) and a correction for this was applied. A total of 1517 reflections was collected to λ^{-1} $\sin\theta$ of 0.616 which after averaging of symmetry-equivalent reflections and rejection of systematic absences gave 1353 of which 1123 (83%) were considered observed using a criterion $I \ge 3.0\sigma(I)$. The crystal data are given in Table 1.

Structure determination and refinement

A consideration of the |E| statistics indicated that $C_{c}^{\frac{2}{c}}$ was the correct space-group choice. A three-dimensional Patterson synthesis located the iron atom on a twofold axis consistent with there being four molecules in the unit cell. This was refined by isotropic least squares and used to phase an electron density map. Two successive cycles of structure factor/electron density syntheses located all the nonhydrogen atoms with R =0.18. Anisotropic refinement and the introduction of a suitable weighting scheme $(w^{-1} = [\sigma(F^2) + (0.04F)^2)$ + 4.01) further reduced R to 0.068. A difference Fourier synthesis was only able to locate a hydrogen close to the nitrogen atom, the positions of the remaining hydrogen atoms being determined from geometric criteria. Further cycles of refinement including the N-H hydrogen atom but excluding the remainder (these were allocated fixed isotropic thermal parameters of B = 5.0 Å²) reduced the R factor to its final value of 0.049 (R_w = (0.070) with the esd of an observation of unit weight = 1.23.

All calculations were carried out on a DEC PDP 11/73 computer using the SDP-PLUS system of crystallographic programs (Frenz, 1983). The final atomic parameters are listed in Table 2.

Discussion

The structure analysis shows the stoichiometry of the compound as $FeCl_2(HpyS)_2$, (the preparation by an alternative route has been reported by Evans and Wil-

Table 2. Positional and thermal parameters with esd's in parentheses"

Atom	x	у	z	$B(\text{\AA}^2)$	U(1, 1)	U(2, 2)	<i>U</i> (3, 3)	<i>U</i> (1, 2)	U(1, 3)	U(2, 3)
Fe	0	0.30760(7)	0.25	3.08(2)	0.0383(3)	0.0400(4)	0.0396(4)	0	0.0140(3)	0
Cl	0.1172(1)	0.4141(1)	0.39633(9)	4.76(3)	0.0642(6)	0.0599(6)	0.0590(6)	-0.0225(5)	0.0233(4)	-0.0188(5)
S	0.1664(1)	0.17391(9)	0.21475(8)	3.40(2)	0.0408(4)	0.0391(5)	0.0517(5)	0.0019(4)	0.0183(3)	0.0026(4)
Ν	0.3734(4)	0.1910(3)	0.1247(3)	3.44(7)	0.036(1)	0.057(2)	0.034(1)	0.007(1)	0.006(1)	0.001(1)
C(1)	0.2815(4)	0.2532(4)	0.1638(3)	2.76(7)	0.027(1)	0.046(2)	0.025(1)	0.001(2)	-0.002(1)	-0.001(2)
C(2)	0.2901(5)	0.3740(4)	0.1591(3)	3.58(8)	0.041(2)	0.048(2)	0.043(2)	-0.009(2)	0.010(1)	-0.005(2)
C(3)	0.3881(5)	0.4252(4)	0.1166(4)	4.3(1)	0.056(2)	0.061(2)	0.042(2)	-0.025(2)	0.008(2)	-0.003(2)
C(4)	0.4818(5)	0.3583(5)	0.0790(3)	4.6(1)	0.040(2)	0.092(3)	0.038(2)	-0.019(2)	0.008(1)	0.003(2)
C(5)	0.4714(5)	0.2410(6)	0.0832(3)	4.31(1)	0.033(2)	0.097(3)	0.031(1)	0.003(2)	0.007(1)	0.001(2)
H(1)	0.372(5)	0.116(4)	0.133(4)	4.3						
H(2)	0.2250	0.4243	0.1873							
H(3)	0.3914	0.5136	0.1123							
H(4)	0.5548	0.3964	0.0494							
H(5)	0.5368	0.1906	0.0540							

^a The temperature factor expression for the nonhydrogen atoms is $exp(-2\pi^2 \{ U_{11} (ha^*)^2 + U_{22} (kb^*)^2 + U_{33} (lc^*)^2 + 2U_{12}ha^*kb + 2U_{13}ha^*lc^* + 2U_{23}kb^*lc^* \}$.



Fig. 1. Stereoview of the structure of $FeCl_2(HpyS)_2$ showing the two halves of the molecule related by a two-fold axis.



Fig. 2. Stereoview of the unit cell packing in FeCl₂(HpyS)₂.

Table 3.	Bond lengths ((Å) and bond	angles (deg.)	with esd's in	parentheses

Atom 1	Atom 2		Distance	Atom 1	Atom 2		Distance
Fe	Cl		2.288(1)	C(3)	C(4)		1.385(8)
Fe	S		2.345(1)	C(4)	C(5)		1.345(9)
S	C(1)		1.722(4)	C(5)	N		1.356(7)
C(1)	C(2)		1.385(6)	N	C(1)		1.356(6)
C(2)	C(3)		1.370(7)	Ν	Н		0.87(5)
C(2)	H(2)		1.01	C(4)	· H(4)		1.00
C(3)	H(3)		1.01	C(5)	H(5)		1.01
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl	Fe	Cl^a	115.79(5)	Ν	C(1)	C(2)	116.7(4)
C1	Fe	S	111.29(4)	C(1)	C(2)	C(3)	120.2(5)
Cl	Fe	S^a	109.20(4)	C(2)	C(3)	C(4)	121.2(5)
S	Fe	S^a	98.76(4)	C(3)	C(4)	C(5)	118.0(5)
Fe	S	C(1)	106.9(1)	N	C(5)	C(4)	120.4(5)
S	C(1)	Ν	116.7(3)	C(1)	N	Н	116(4)
S	C(1)	C(2)	126.6(4)	C(5)	Ν	Н	121(4)

^{*a*}Symmetry operators: -x, y, $\frac{1}{2} - z$.

kinson, 1974) instead of the desired mixed ligand complex $FeCl_2(pyS)(Ph_3P)_2$.

The molecule possesses twofold symmetry, the geometry about Fe(II) is distorted tetrahedral with bond

angles varying in the range 98.76(4)° for S–Fe–S to 115.78(4)° for Cl–Fe–Cl, the latter being increased presumably to minimize repulsion, Table 3. Of interest is the mode of coordination of the C_5H_5NS ligand which

is coordinated only through the S atom at a Fe–S distance of 2.345(1) Å. This distance is shorter than that found in (Et₄N)[Fe(pyS)₃] (average 2.568(1) Å) (Rosenfield *et al.*, 1986) but longer than those in (C₅H₄N)(CO)₆Fe₂--(μ_4 -S)-Fe(CO₆)(pyS) (2.236(2) - 2.286(2) Å) (Bargue and Grandjean, 1975).

The C₅H₅NS ligand is planar [maximum deviation .01 Å and the S atom lies -0.020(1) Å below this plane. The plane of the ligand lies such as to almost bisect the Cl—Fe—Cl* angle, the torsion angle Fe—S—C(1)—N being -171.3. The S—C(1) distance of 1.722(4) Å is much longer than the value of 1.692(2) Å found in the free ligand (Ohms *et al.*, 1982) and lies toward the top end of the range found in other structurally characterized complexes of the thione ligand (Binamira-Soriaga *et al.*, 1979; Deeming *et al.*, 1986; Valle *et al.*, 1987) where it has been proposed that complexation in the zwitterionic form (3) as opposed to the thione form (1) is responsible for this effect (Lobana *et al.*, 1989).



Of note is the formation of an intermolecular N-H \cdots Cl hydrogen bond (N \cdots Cl 3.178(5) Å) as opposed to an intramolecular type which has been observed in the complex [CuCl(C₆H₅NS)(PPh₃)₂] (Lobana *et al.*, 1989). In this particular instance, there seems to be no steric reason why rotation about the S-C(1) bond could not bring the NH group into sufficiently close proximity to the Cl atom for hydrogen bond formation to occur and it is likely that an increase is packing efficiency is favored by the formation of this intermolecular bonding which leads to a linking of adjacent molecules forming chains running approximately parallel to *a*. This manifests itself in a small increase in the Fe–Cl distance of 2.288(1) Å compared to a value of 2.24(1) Å found in a similar tetrahedral complex cis–[Fe(phen₂)Cl₂] (Figgis *et al.*, 1983).

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References

- Bargue, G., and Grandjean, D. (1975) J. Orgamomet. Chem., 92, 381.
- Binamira-Soriaga, E., Lundeen, M., and Seff, K. (1979) Acta Crystallogr. B35, 2875.
- Castineiras, A., Hiller, W., Strahle, J., Bravo, J., Casas, J. S., Gayoso, M., and Sordo, J. (1986) J. Chem. Soc. Dalton Trans., 1945.
- Deeming, A. J., Meah, M. N., Dawes, H. M., and Hursthouse, M. B. (1986) J. Organomet. Chem. C25, 299.
- Evans, I. P., and Wilkinson, G. (1974) J. Chem. Soc. Dalton Trans. 1946.
- Figgis, B. N., Patrick, J. M., Reynolds, P. A., Skelton, B. W., White, A. H., and Healy, P. C. (1983) *Aust. J. Chem.* **36**, 2043.
- Jezierski, A., and Jezowska-Trazeloiatowska, B. (1984) Polyhedron 3, 1065.
- Kinoshita, I., Yasuba, Y., Matsumoto, K., and Ooi, S. (1983) Inorg. Chem. Acta 80, L13.
- Lobana, T. S., Bhatia, P. K., and Tiekink, E. R. T. (1989) J. Chem. Soc. Dalton Trans. 749.
- Lobana, T. S., and Bhatia, P. K. (1990) Coord. Chem. Rev. (submitted).
- Mura, P., Olby, B. G., and Robinson, S. D. (1985) J. Chem. Soc. Dalton Trans., 2101.
- Ohms, U., Guth, H., Kutoglu, A. and Scheringer, C. (1982) Acta Crystallogr. B38, 831.
- Raper, E. S. (1985) Coord. Chem. Rev. 61, 115.
- Rosenfield, S. G., Swedberg, S. A., Arora, S. K., and Mascharak, P. K. (1986) Inorg. Chem. 25, 2109.
- SDP structure determination package, Ver 1.1a (1983) B. A. Frenz and Associates Inc., College Station, Texas.
- Valle, G., Ettorre, R., Vettori, U., Peruzzo, V., and Plazzogna, G. (1987) J. Chem. Soc. Dalton Trans. 815.

Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60696 (5 pages).