Metal Dithiocarbamates and Related Complexes. Part 2.[1] Reactions of Iron Complexes with Lewis Bases and with Zinc Iodide, and the Structure of $[Fe\{CN(\textit{p}\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$

By **Jon A. McCleverty,*** **Sarah McLuckie, Norman J. Morrison, Neil A. Bailey,*** and **N. W. (Joe) Walker,**
Chemistry Department, The University, Sheffield S3 7HF

Reactions of $[Fe(S_2CNEt_2)_3]^{+,0}$, $[FeI(S_2CNEt_2)_2]$, and $[Fe(S_2CNEt_2)_2]$ with $Ph_2PCH_2CH_2PPh_2$ (dppe), CNR, and PPh_3 are described. The complexes $[Fe(dppe)(S_2CNEt_2)_2]^{+,0}$, $[Fe(CNR)_2(S_2CNEt_2)_2]^z$ ($z = +1$, R = p-ClC_6H_4; $z = 0$, R = Pr^i, Bu^t, or p-ClC_6H_4), and $[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)]^+$ were characterised analytically, spectrally, and voltammetrically. Treatment of $[Fe(S_2CNEt_2)_3]^+$ with PPh_3 afforded $[Fe(S_2CNEt_2)_3]$, PPh_3S, and $[PPh_3\{C(NEt_2)S\}]^+$. An equilibrium is established, under nitrogen, between mixtures of $[Fe(S_2CNEt_2)_3]$ and ZnI_2 with $[FeI(S_2CNEt_2)_2]$ and $[Zn(S_2CNEt_2)_2]$; in air, the first two afforded, *inter alia* $[ZnI_2(Et_2NCS_2)_2]$.

$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ reacted with ZnI_2 giving $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$. An *X*-ray crystallographic examination of this compound revealed that it had crystallographically imposed C_2 symmetry, the Fe atom having a distorted octahedral geometry consisting of two mutually *cis* p-ClC_6H_4NC groups and two bidentate dithiocarbamato-ligands. One sulphur atom of each S_2CNEt_2 group formed a bridge to the zinc atom, the distorted tetrahedral geometry of which was completed by the two iodine atoms. The relationship of this structure to the possible mechanism of ligand exchange between $[Fe(S_2CNEt_2)_3]$ and ZnI_2 is briefly discussed.

WE, and others, have observed [1,2] that oxidised nickel dithiocarbamates, $[Ni(S_2CNR_2)_3]^+$ (formally described as containing Ni^{IV}), readily react with tertiary phosphines and isonitriles (L) giving $[Ni(S_2CNR_2)L_2]^+$ and liberating the tetra-alkylthiuram disulphide, $(R_2NCS_2)_2$. These reactions appear to involve a two-electron internal redox process whereby two dithiocarbamato-ligands are oxidised to the thiuram disulphide, which is displaced by L, and the metal, concomitantly, is reduced from Ni^{IV} to Ni^{II}.

In seeking to establish the generality of this type of reaction, we have extended our studies of the reactions of tertiary phosphines and isocyanides with metal dithiocarbamates to the iron complexes $[Fe(S_2CNR_2)_3]^z$, where $z = +1$ (ref. 3) or 0. Displacement of thiuram disulphide from the Fe^{IV} complex might be expected, but the relative ease of one-electron reduction of this species to the well-characterised Fe^{III} species prompted our investigations of its reactions with Lewis bases also. It is known that iron(II) bis(dithiocarbamates) react with CO [4] and *o*-phenanthroline,[5] forming $[Fe(CO)_2(S_2CNR_2)_2]$ and $[Fe(o\text{-}phen)(S_2CNR_2)_2]$, and so reactions of $[Fe(S_2CNEt_2)_2]$ with $Ph_2PCH_2CH_2PPh_2$ and isocyanides have also been included in this study.

A preliminary account of some of this work has been published.[6]

RESULTS AND DISCUSSION

Reactions of the Fe^{IV} *Complexes.*—Treatment of black $[Fe(S_2CNEt_2)_3][BF_4]$ with p-ClC_6H_4NC afforded the yellow $[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)]^+$, and white crystals of $(Et_2NCS_2)_2$ (analytical and conductivity data are given in Table 1). In fact this reaction is the only one we have found in this investigation which parallels the behaviour of the Ni^{IV} species. Unlike the nickel system, the iron(II) species produced is, of course, six-co-ordinate.

Reaction with PPh_3 gave, as expected from our previous work, Ph_3PS, $[Ph_3P\{C(NEt_2)S\}][BF_4]$, and $[Fe(S_2CNEt_2)_3]$. With an excess of PPh_3, after long periods, a red insoluble solid was produced but our attempts at characterisation failed. At no time could we obtain evidence of the existence of $[Fe(PPh_3)_n(S_2CNEt_2)_m]^+$ ($n = 2$, $m = 2$ or $n = 4$, $m = 1$).

With $Ph_2PCH_2CH_2PPh_2$ (dppe) (in a 1 : 1 or 1 : 2 molar ratio) the Fe^{IV} cation afforded $[Fe(dppe)(S_2CNEt_2)_2][BF_4]$. This is an unusual reaction since it formally represents a one-electron reduction of Fe^{IV} to Fe^{III} with concomitant loss of a dithiocarbamyl radical. In an analogous reaction with dppe, $[Co_2(S_2CNEt_2)_5][BF_4]$ afforded red $[Co(dppe)(S_2CNEt_2)_2][BF_4]$.

Treatment of $[Fe(S_2CNEt_2)_3]^+$ with $PMePh_2$ in air led to the formation of $P(:O)MePh_2$ and $[Fe(S_2CNEt_2)_3]$, but we were unable to isolate $[Fe(PMePh_2)_n(S_2CNEt_2)_m]^+$.

Reactions with Fe^{III} *Complexes.*—Reaction of $[Fe(S_2CNEt_2)_3]$ with RNC in the absence of air and light afforded the Fe^{II} complexes $[Fe(CNR)_2(S_2CNEt_2)_2]$ (R = Pr^i, Bu^t, or p-ClC_6H_4); $(Et_2NCS_2)_2$ was recovered from the reaction mixture. Here again, a one-electron redox process has occurred, the thiuram disulphide presumably being formed by dimerisation of the liberated dithiocarbamyl radical.

The ease of this reaction was unexpected, but could be extended to other Lewis base systems. Thus, treatment of $[Fe(S_2CNEt_2)_3]$ with dppe in refluxing acetone afforded $[Fe(dppe)(S_2CNEt_2)_2]$ (isolated as an acetone solvate) together with dppe dioxide and other uncharacterised by-products. There was no spectroscopically detectable reaction between $[Fe(S_2CNEt_2)_3]$ and CO in solution in refluxing acetone after 4 h, but after 3 days in the cold, substantial amounts of $[Fe(CO)_2(S_2CNEt_2)_2]$ could be detected. This type of dicarbonyl has been obtained by carbonylation [4] of $[Fe(S_2CNR_2)_2]$ or treatment of $[Fe(CO)_4I_2]$ with $[S_2CNR_2]^-$.[7]

A reaction occurred when p-ClC_6H_4NC was added to

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[1] Part 1, J. A .McCleverty and N. J. Morrison, *J.C.S. Dalton*, 1976, 541.

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[3] E. A. Pasek and D. K. Straub, *Inorg. Chem.*, 1972, **11**, 259.

[4] H. Buttner and R. D. Feltham, *Inorg. Chem.*, 1972, **11**, 971.

[5] B. L. Edgar, D. J. Duffy, M. L. Palazzotto, and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1973, **95**, 1125.

[6] A. K. M. Groves, N. J. Morrison, and J. A. McCleverty, *J. Organometallic Chem.*, 1975, **84**, C5.

[7] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.

$[FeI(S_2CNEt_2)_2]$, and in the presence of $Tl[PF_6]$, $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2][PF_6]$ was formed. Reaction of $[FeI(S_2CNEt_2)_2]$ with dppe and $K[PF_6]$ afforded $[Fe(dppe)(S_2CNEt_2)_2][PF_6]$.

Reaction of Fe^{II} *Complexes*.—Reaction of $[Fe(S_2CNEt_2)_2]$ with $p\text{-}ClC_6H_4NC$ afforded $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ and, with dppe, $[Fe(dppe)(S_2CNEt_2)_2]$ could be obtained. Attempts to obtain compounds containing PPh_3 were unsuccessful.

Oxidation of $[Fe(dppe)(S_2CNEt_2)_2]$ to the monocation, already discussed above, was readily achieved using HPF_6 in air. This reaction is entirely consistent with the electrochemical properties of the starting material (see below).

Electrochemical Studies.—It appears that most six-co-ordinate iron complexes containing only charged sulphur donor ligands exist [8,9] predominantly within a three-membered electron-transfer series, corresponding formally to the metal oxidation states IV, III, and II. Replacement of some of these ligands by Lewis bases might be expected to attenuate the redox series or to increase the oxidative (π-acceptor bases) or reductive (donor bases) stability of the central member of the series.

Voltammetric studies of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ in dichloromethane revealed (Table 2) only one (anodic) wave, corresponding to the formation of the monocation. The potential for the formation of this species indicated that the monocation would be very susceptible to reduction by even weakly basic solvents, as observed. The potential for the oxidation of $[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)]^+$ was very positive, as expected for a species having a positive charge and carrying π-acceptor ligands. No attempt was made to prepare the dication.

One-electron oxidation and reduction of $[Fe(dppe)(S_2CNEt_2)_2]^+$ was detected voltammetrically, the oxidation step again requiring, as was anticipated, a very positive potential. Oxidation of $[Fe(dppe)(S_2CNEt_2)_2]$ to the monocation occurred at a negative potential, and so the chemical formation of $[Fe(dppe)(S_2CNEt_2)_2]^+$ was achieved easily (see above).

Spectral Properties.—The i.r. spectra of $[Fe(CNR)_2(S_2CNR_2)_2]^{0,+}$ are characterised, *inter alia*, by bands due to co-ordinated isocyanide (see Table 3). When R = Bu^t, two absorptions were observed, consistent with the overall *cis*-geometry of the complexes. However, when $R = p\text{-}ClC_6H_4$ or Pr^i, three bands were observed in solution in the region 2 000—2 100 cm^{-1}. On symmetry grounds, only two are expected, and the occurrence of a mixture of *cis*- and *trans*-isomers was dismissed on the basis of ^1H n.m.r. spectral studies (Table 3) in the same solvent in which the i.r. spectral data were obtained. The extra band probably arises because of Fermi resonance effects. The frequency, ν_1, responsible for the overtone which mixes with a symmetry equivalent vibration, ν_2 (2 037 cm^{-1}) was expected to be close to, and found to occur at, 1 011 cm^{-1} (the three frequencies observed occurred at 2 008, 2 045, and 2 094 cm^{-1}). In these isonitrile complexes, $\nu(CN)$ occurred at frequencies lower than that in the free ligand, indicating that $d_\pi \longrightarrow \pi^*$ donation was occurring from the metal to isocyanide ligand. As expected, $\nu(CN)$ was higher in the monocations than in the neutral species.

In the cationic species, $[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)_2]^+$, $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]^+$, and $[Fe(dppe)(S_2CNEt_2)_2]^+$, $\nu(C-N)$ of the $S_2C\text{-}NEt_2$ group occurred at, or above, 1 506 cm^{-1}, whereas in the neutral complexes it occurred below 1 495 cm^{-1}. This is presumably because there is greater mesomeric release of electron density from the NEt_2 group in the cationic compounds than in the neutral species.

The neutral complexes $[Fe(dppe)(S_2CNEt_2)_2]$ and $[Fe(CNR)_2(S_2CNEt_2)_2]$, and also $[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)]^+$, exhibited sharp ^1H n.m.r. spectral signals in the expected regions (Table 3) consistent with their diamagnetism, *cisoid* geometries, and stereochemical rigidity at room temperature. The proton signals of the ethyl groups in $[Fe(CNR)_2(S_2CNEt_2)_2]$ and $[Fe(dppe)(S_2CNEt_2)_2]$ appeared as two overlapping quartets and two overlapping triplets, consistent with the proposed rigid structures of the compounds.* However, in $CDCl_3$, the methylenic protons appeared as a complex multiplet, possibly as a result of interaction with the solvents, such as occurs with $[Co(S_2CNEt_2)_3]$.[10,†] The sharp and normal ^1H n.m.r. spectrum of $[Co(dppe)(S_2CNEt_2)_2]^+$ confirmed that the compound is diamagnetic, with an octahedral structure.

Reactions of Iron Dithiocarbamate Complexes with Zinc Halides.—In the reaction between $[Fe(S_2CNEt_2)_3]$ and RNC, tetraethylthiuram disulphide is eliminated. Separation of this from the product $[Fe(CNR)_2(S_2CNEt_2)_2]$ proved to be difficult on some occasions, and in an attempt to remove the disulphide as a crystalline solid the reaction mixture was treated with ZnI_2 (in the hope of obtaining

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* It has been observed (M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, jun., and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1973, **95**, 4537 and ref. 5) that high-spin iron complexes *viz.*, $[Fe(phen)(S_2CNEt_2)_2]$ ($S = 2$) have much lower barriers to intramolecular rearrangements than low-spin compounds. The diamagnetic $[Fe(CO)_2(S_2CNEt_2)_2]$, $[Fe(CNR)_2(S_2CNEt_2)_2]$, and $[Fe(dppe)(S_2CNEt_2)_2]$ are stereochemically rigid at room temperature, whereas for $[Fe(phen)(S_2CNEt_2)_2]$ and its analogues, ΔG for metal-centred inversion is <7 kcal mol^{-1} (at -100 °C) and for C–N bond rotation is between 8 and 9 kcal mol^{-1} (between -70 and -80 °C). At $+50$ °C in C_2Cl_4, the ^1H n.m.r. spectrum of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ contained two broad singlets in the range $\delta = 1$—3 p.p.m.; at $+90$ °C, these had become a sharp singlet).

† Unusual shifts in the methylene-proton resonances of $[Co(S_2CNEt_2)_3]$ have been observed in $CDCl_3$. These, and the spectral effect reported herein, could arise from the kind of solvent interactions detected by *X*-ray crystallographic studies of dichloromethane- and chloroform-solvated tris(morpholino)-dithiocarbamate complexes, $[M(S_2C\overline{NCHCH_2OCH_2C}H_2)_3]$ ($M =$ Fe or Co) (P. C. Healy and E. Sinn, *Inorg. Chem.*, 1975, **14**, 109).

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TABLE 1

Analytical, m.p., and conductivity data obtained from dithiocarbamato and related compounds

	Analytical results (%)											
	Found					Calculated						
Complex	C	H	N	S	Hal	C	H	N	S	Hal	M.p. (θ_c/°C)	Λ [a]
$[Fe(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2][BF_4]$	51.6	5.5	3.2			51.6	5.3	3.5			190	84
$[Fe(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2][PF_6]$	48.6	4.9	3.1	14.3		48.0	4.9	3.1	14.2			
$[Fe(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2]\cdot Me_2CO$	57.6	6.2	3.5	17.1		57.9	6.2	3.5	15.8			
$[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)][BF_4]$	46.9	3.2	8.6		17.0	47.1	3.1	8.3		16.9	122	86
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2][PF_6]$	37.3	3.6	7.3	16.6	9.2	37.0	3.7	7.0	16.5	9.4		
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$	46.3	4.7	9.0	20.4	11.4	45.9	4.5	8.9	20.4	11.3		0
$[Fe(CNBu^t)_2(S_2CNEt_2)_2]$	46.7	7.2	10.9	24.4		46.4	7.3	10.9	24.7		105d	0
$[Fe(CNPr^i)_2(S_2CNEt_2)_2]$	44.1	6.9	11.4	26.1		43.6	7.1	11.5	26.7			
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$	30.5	3.0	5.9	13.7	7.5 [b]	30.4	3.0	5.9	13.5	7.5 [b]		
$[PPh_3\{C(NEt_2)S\}][BF_4]$	59.3	5.7	2.9			59.4	5.4	3.0			147	84
$P(\dot{:}O)MePh_2$	72.2	6.0				72.2	6.3					

[a] Conductivity in 1×10^{-3} mol dm^{-3} $MeNO_2$ solution, in S cm^2 mol^{-1}; for a 1 : 1 electrolyte, Λ = 80—100. [b] I analysis: Found 26.8, Calc., 26.8%.

TABLE 2

Voltammetric data obtained from iron dithiocarbamate complexes

	Voltammetry			Cyclic voltammetry [d]		
Complex	$E_{\frac{1}{2}}$ [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ [b]	D [c]	E_{pa}	E_{pc}	ΔE [d]
$[Fe\{(CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$	0.44	90	9.9	0.465	0.320	145
$[Fe\{(CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)][BF_4]$	1.53	90	14.6	1.555	1.415	140
$[Fe(dppe)(S_2CNEt_2)_2][BF_4]$	1.01	76	8.5	1.045	0.925	120
	−0.25	85	8.9	−1.450	−0.290	145

[a] In volts *vs.* S.C.E. at a rotating Pt electrode in CH_2Cl_2. [b] Reversibility criterion in mV; for a reversible one-electron process, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 59$ mV. [c] $D = i_d/c$ in μA mmol^{-1} (calculated for $n = 1$); for the one-electron process $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^- + e^-$, $D = 10.8$ at the electrode used in this work. [d] $E_{pa} - E_{pc}$ in mV. For a reversible process $\Delta E \simeq 130$ mV.

TABLE 3

I.r. and n.m.r. spectral data obtained from iron dithiocarbamates and their derivatives

	I.r. data (cm^{-1}) [a]		^1H N.m.r. data [b]			
Complex	ν(C–N)	ν(C≡N)	δ	(A) [c]	mult. [d]	Assignment
$[Fe\{CN(p\text{-}ClC_6H_4)\}_4(S_2CNEt_2)]^+$	1 506	2 128sh	7.44	(8)	m	$C_6\mathit{H}_4$
		2 146	3.77	(2)	q	$N(C\mathit{H}_2Me)_2$
		2 189	1.30	(3)	t	$N(CH_2C\mathit{H}_3)_2$
$[Fe(CNPr^i)_2(S_2CNEt_2)_2]$	1 486	2 037	6.01	(5)	m	$C\mathit{H}Me_2$
		2 072	6.34		q	$N(C\mathit{H}_2Me)_2$
		2 114	8.59	(6)	d	$CH(C\mathit{H}_3)_2$
			8.79	(6)	t	$N(CH_2C\mathit{H}_3)_2$
$[Fe(CNBu^t)_2(S_2CNEt_2)_2]$	1 487	2 042	3.80	(4)	m	$N(C\mathit{H}_2Me)_2$
		2 109	1.47	(9)	s	$C(C\mathit{H}_3)_3$
			0.25	(6)	t	$N(CH_2C\mathit{H}_3)$
			0.18		t	$N(CH_2C\mathit{H}_3)$
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$	1 492sh	2 008	7.25	(2)	s	$C_6\mathit{H}_4$
		2 045	2.81	(2)	q [e]	$N(C\mathit{H}_2Me)_2$
		2 093	1.23	(3)	t	$N(CH_2C\mathit{H}_3)_2$
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]^+$	1 500	2 128sh	7.44	(8)	m	$C_6\mathit{H}_4$
		2 146	3.77	(2)	q	$N(C\mathit{H}_2Me)_2$
		2 189	1.30	(3)	t	$N(CH_2C\mathit{H}_3)_2$
$[Fe(dppe)(S_2CNEt_2)_2]$ [f]	1 485		7.23	(10)	m	$\{P(C_6\mathit{H}_5CH_2\}_2$
			3.30	(6)	m	$N(C\mathit{H}_2Me)_2 + \{PPh_2C\mathit{H}_2\}_2$
			2.11	(3)	s	$(C\mathit{H}_3)_2CO$
			0.82	(6)	m	$N(CH_2C\mathit{H}_3)_2$
$[Fe(dppe)(S_2CNEt_2)_2]^+$	1 510 [g]					
$[Co(dppe)(S_2CNEt_2)_2]^+$	1 508 [g]		7.66 [h]	(5)	m	$\{P(C_6\mathit{H}_5)_2CH_2\}_2$
			3.33	(3)	m	$N(C\mathit{H}_2Me)_2 + \{PPh_2C\mathit{H}_2\}_2$
			0.95	(3)	t	$N(CH_2C\mathit{H}_3)$
			0.80		t	$N(CH_2C\mathit{H}_3)$
$[PPh_3\{C(NEt_2)S\}]^+$	1 482		7.75	(15)	m	$P(C_6\mathit{H}_5)_3$
			4.16	(2)	q	$N(C\mathit{H}_2Me)$
			3.69	(2)	q	$N(C\mathit{H}_2Me)$
			1.40	(3)	t	$N(CH_2C\mathit{H}_3)$
			0.55	(3)	t	$N(CH_2C\mathit{H}_3)$
$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$	1 516	2 079				
		2 122				

[a] CH_2Cl_2 soln. [b] $CDCl_3$ soln. at 100 MHz (30 °C). [c] Relative area. [d] Multiplicity of peaks. [e] Not completely resolved. [f] Acetone solvate. [g] KBr disc. [h] $(CD_3)_2CO$ solution.

$[ZnI_2(Et_2NCS_2)_2]$. However, in acetone solution, a deep red solid was obtained, which could also be produced by direct reaction of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ with zinc iodide. This material, the analysis for which agreed with its formulation as $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$, was insufficiently soluble for n.m.r. spectral or molecular-weight measurements. However, in dichloromethane solution, the i.r. spectrum exhibited bands characteristic of co-ordinated isocyanide and dithiocarbamate, and clearly ruled out the existence of the anion $[ZnI_2(S_2CNEt_2)]^-$.[11] An *X*-ray crystallographic examination of this compound, which is described in the next section, confirmed our formulation, and revealed that the adduct contained six-co-ordinate iron and four-co-ordinate zinc bridged by the dithiocarbamate ligands.

The observation that $[Fe(CNR)_2(S_2CNEt_2)_2]$ readily formed a 1 : 1 adduct with the Lewis acid ZnI_2 prompted our examination of the behaviour of $[Fe(S_2CNEt_2)_3]$ with ZnX_2.

Addition of ZnI_2 (1 mol equiv.) to $[Fe(S_2CNEt_2)_3]$ (2 mol equiv.) in acetone *in air* readily afforded purple-black solutions from which $[Fe(S_2CNEt_2)_3]$ was recovered (in reduced amounts relative to the initial quantity used) together with $[ZnI_2(R_2NCS_2)_2]$, and a brown, insoluble, and only partly characterised solid (A). When the reaction was carried out under *nitrogen*, however, $[FeI(S_2CNEt_2)_2]$ was obtained, and although not actually isolated, $[Zn(S_2CNEt_2)_2]$ was presumably formed. These data imply that, on mixing the reactants, an equilibrium is established, *viz*.

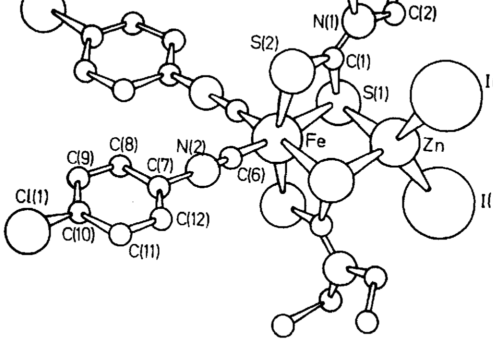
$$2[Fe(S_2CNEt_2)_3] + ZnI_2 \rightleftharpoons 2[FeI(S_2CNEt_2)_2] + [Zn(S_2CNEt_2)_2],$$

and that this equilibrium is upset by exposure of the reaction mixture to air, thus leading to the formation of oxidised products.

Support for this hypothesis is gained from spectrophotometric and synthetic studies. Thus, mixtures of $[Fe(S_2CNEt_2)_3]$ with ZnI_2 and of $[FeI(S_2CNEt_2)_2]$ with $[Zn(S_2CNEt_2)_2]$ at appropriate concentrations in acetone under nitrogen gave electronic spectra with shoulders at *ca*. 500 and 600 nm. The establishing of the equilibria was monitored with time and it was observed that while equilibration occurred very rapidly, the concentration of the absorbing species decreased with time, and small amounts of a brown powder precipitated in the spectral cells. This may be attributed to oxidation of the products by traces of air present in the solvent or in the nitrogen gas passed over the cells. On mixing $[FeI(S_2CNEt_2)_2]$ with $[Zn(S_2CNEt_2)_2]$ *in air*, the species $[Fe(S_2CNEt_2)_3]$, $[ZnI_2(Et_2NCS_2)_2]$, and a light brown powder, which has an i.r. spectrum similar to the brown material (A) mentioned above, were obtained. When $[Fe(S_2CNEt_2)_3]$ was treated with $ZnBr_2$ (2 : 1 stoicheiometry), the products included $[Fe(S_2CNEt_2)_3]$, $[ZnBr_2(Et_2NCS_2)_2]$, and $[FeBr(S_2CNEt_2)_2]$. Using $ZnCl_2$ in place of the bromide, only $[Fe(S_2CNEt_2)_3]$ and $[FeCl(S_2CNEt_2)_2]$ could be isolated.

In view of the formation of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$ it is tempting to conclude that intermediates involving adducts of $[Fe(S_2CNEt_2)_3]$ and ZnX_2 are involved in the reactions described above. These intermediates could be of the 1 : 1 or 2 : 1 type, and the latter, formally represented as $[\{Fe(S_2CNEt_2)_3\}_2ZnX_2]$ could rearrange in two ways: either by reversible transfer of X to Fe and (S_2CNEt_2) to Zn in the absence of air thereby giving a mixture of $[Fe(S_2CNEt_2)_3]$, ZnX_2, $[Fe(S_2CNEt_2)_2X]$, and $[Zn(S_2CNEt_2)_2]$; or, in the presence of air, irreversibly breaking down into $[Zn(Et_2NCS_2)_2X_2]$ and $[Fe(S_2CNEt_2)_2]$, the last being oxidised to $[Fe(S_2CNEt_2)_3]$ and presumably oxy- or hydroxy-dithiocarbamate complexes [perhaps (A)?]. Indeed, the brown powders observed in those reactions carried out in air exhibited ν(OH) and bands due to co-ordinated dithiocarbamate. However, we were unable to purify these powders, and so elemental analyses of the compounds were unreliable.

Structure of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$.—Data relevant to the crystal and molecular structure determination are given in the Experimental section.



FIGURE

The structure of the compound with the atom numbering scheme is shown in the Figure; bond lengths and angles are listed in Tables 4 and 5, respectively.

The molecule has crystallographically imposed C_2 symmetry with the iron and zinc atoms on the C_2 axis. The essential features of the structure are that the iron has a distorted octahedral environment and the zinc a distorted tetrahedral geometry, the metals atoms being bridged by two symmetry-related sulphur atoms of the S_2CNEt_2 ligands which are bidentate with respect to the Fe atom. The co-ordination sphere of the iron atom is completed by two mutually *cis* symmetry-related *p*-chlorophenyl isocyanide ligands; the zinc atom carries two symmetry-equivalent terminal iodine atoms.

The Zn–I bond length [2.552(3) Å] is in the range expected,[12] and is very close to the values [2.560(1) and

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2.541(2) Å] found in $[\mathrm{ZnI_2(Me_2NCS_2)_2}]$.[13] The Zn–S(1) bridging bond length [2.422(5) Å] is slightly longer than most Zn–S distances found in other zinc dithiocarbamates,[14] but is shorter than Zn · · · S interactions of weaker nature (2.65—3.0 Å) such as are found in five- and six-co-ordinate systems.[15]

TABLE 4

Bond lengths (Å) obtained from $[\mathrm{Fe\{CN(\textit{p}\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2}]$

Zn–I(1)	2.552(3)	C(4)–C(5)	1.560(27)
Zn–S(1)	2.422(5)	C(6)–N(2)	1.151(22)
Fe–S(1)	2.374(5)	N(2)–C(7)	1.365(22)
Fe–S(2)	2.305(6)	C(7)–C(8)	1.438(23)
Fe–C(6)	1.832(17)	C(7)–C(12)	1.329(24)
S(1)–C(1)	1.757(17)	C(8)–C(9)	1.371(23)
S(2)–C(1)	1.703(17)	C(9)–C(10)	1.385(23)
C(1)–N(1)	1.327(21)	C(10)–C(11)	1.416(26)
N(1)–C(2)	1.488(22)	C(11)–C(12)	1.431(26)
N(1)–C(4)	1.502(21)	Cl(1)–C(10)	1.723(18)
C(2)–C(3)	1.487(29)		

TABLE 5

Bond angles (°) obtained from $[\mathrm{Fe\{CN(\textit{p}\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2}]$

I(1)–Zn–I(1′)	118.4(1)	S(1)–C(1)–N(1)	123.8(12)
I(1)–Zn–S(1)	110.2(1)	S(2)–C(1)–N(1)	125.7(13)
I(1)–Zn–S(1′)	112.7(1)	C(1)–N(1)–C(2)	120.2(13)
S(1)–Zn–I(1′)	112.7(1)	C(1)–N(1)–C(4)	120.6(13)
S(1)–Zn–S(1′)	88.8(2)	C(2)–N(1)–C(4)	119.1(13)
S(1)–Fe–S(1′)	91.2(2)	N(1)–C(2)–C(3)	112.5(15)
S(1)–Fe–S(2)	74.8(2)	N(1)–C(4)–C(5)	111.4(14)
S(1)–Fe–C(6)	171.5(6)	Fe–C(6)–N(2)	177.6(15)
S(1)–Fe–S(2′)	95.3(2)	C(6)–N(2)–C(7)	172.5(17)
S(1)–Fe–C(6′)	91.9(5)	N(2)–C(7)–C(8)	117.8(14)
S(2)–Fe–S(2′)	166.2(2)	N(2)–C(7)–C(12)	120.5(15)
S(2)–Fe–C(6)	97.0(6)	C(8)–C(7)–C(12)	121.6(15)
S(2)–Fe–C(6′)	93.1(5)	C(7)–C(8)–C(9)	120.4(15)
C(6)–Fe–C(6′)	86.4(8)	C(8)–C(9)–C(10)	117.9(15)
Zn–S(1)–Fe	90.0(2)	C(9)–C(10)–C(11)	122.7(16)
Zn–S(1)–C(1)	96.8(6)	C(9)–C(10)–Cl(1)	119.3(13)
Fe–S(1)–C(1)	85.6(6)	C(11)–C(10)–Cl(1)	118.0(14)
Fe–S(2)–C(1)	89.0(6)	C(10)–C(11)–C(12)	117.6(17)
S(1)–C(1)–S(2)	110.5(9)	C(11)–C(12)–C(7)	119.7(16)

Primed atoms are related by the C_2 axis.

The Fe–S bond lengths [2.374(5) and 2.305(6) Å] are similar to the values found[16] in $[\mathrm{Fe(S_2CNEt_2)_3}]$; the longer of the two bonds, Fe–S(1), being associated with the bridging arrangements; the C–S distances [1.757(17) and 1.703(17) Å] show a similar variation. With the exception of the longer C–S bond, the geometry of the dithiocarbamato-ligands is similar to that found in $[\mathrm{Fe(S_2CNEt_2)_3}]$. The $\{\mathrm{S_2CNC_2}\}$ fragment is relatively planar (root-mean-square deviation 0.029 Å) but the deviations are perhaps slightly larger than normal (maximum 0.039 Å) with the iron atom only 0.032 Å out of the plane.

The isocyanide ligand consists of a planar phenyl ring (root-mean-square deviation 0.009 Å) with coplanar substituents. The Fe–C(6) bond length [1.832(17) Å] is slightly shorter than that [1.874(3) Å] found[17] in $[\mathrm{Fe(CNMe)_6}]^{2+}$, owing to the greater electron-withdrawing power of the p-$\mathrm{ClC_6H_4}$ ligand and to the greater opportunity for back-donation to the isocyanide ligand. The Fe–C(6)–N(2)–C(7) unit is, as expected, almost linear, and the bond lengths within the isonitrile ligand are very similar to those found[18] from the rather inaccurate structural determination of $[\mathrm{FeBr(CO)_3(CNPh)_2}]$ [C–N 1.12(4), N–C(P) 1.39(8) Å]. It can be seen from the Figure that the phenyl rings are almost coplanar with the $\mathrm{FeS_2Zn}$ bridge system.

X-Ray structural analyses of salts of the cations $[\mathrm{M_2(S_2CNR_2)_5}]^+$ (M = Co, R = Et; M = Ru, R = $\mathrm{Pr^i}$) have revealed[19] that these cations may be considered as an octahedral $\mathrm{M(S_2CNR_2)_3}$ unit co-ordinated in the *cis*-position of a octahedral $[\mathrm{M(S_2CNR_2)_2}]^+$ species of opposite chirality. These observations, together with the isolation and structural characterisation of $[\mathrm{Fe\{CN(\textit{p}\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2}]$, suggest that metal complexes containing adjacent dithiocarbamate groups may function as chelating ligands,* and provide support for the mechanism of ligand exchange between $\mathrm{ZnI_2}$ and $[\mathrm{Fe(S_2CNEt_2)_3}]$.

EXPERIMENTAL

The compounds $[\mathrm{Fe(S_2CNEt_2)_3}][\mathrm{BF_4}]$ and $[\mathrm{FeI(S_2CNEt_2)_2}]$ were prepared as described in the literature, but a modification of the synthesis of the former was developed (see below). Yields are quoted relative to the metal-containing starting material and melting points are uncorrected. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

Voltammetric results were obtained using an Electroscan 30 Polarograph, with a rotating Pt electrode (620 r.p.m.). The complex was 1×10^{-3} mol dm^{-3} in dichloromethane, $[\mathrm{Et_4N}][\mathrm{ClO_4}]$ (5×10^{-2} mol dm^{-3}) was base electrolyte, and the data were collected at 22 °C using a three-electrode configuration.

I.r. spectral data were obtained using PE180 and 457 spectrophotometers, and ^{1}H n.m.r. spectra using a Varian HA 100 instrument. U.v. and visible spectral information was obtained using a Cary-14 spectrophotometer.

$[\mathrm{Fe\{CN(\textit{p}\text{-}ClC_6H_4)\}_4(S_2CNEt_2)}][\mathrm{BF_4}]$.—A solution of $[\mathrm{Fe(S_2CNEt_2)_3}][\mathrm{BF_4}]$ (1.18 g, 2 mmol) in acetone (20 cm^3) was mixed with a solution of p-$\mathrm{ClC_6H_4NC}$ (0.55 g) in the same solvent (10 cm^3). The solution was set aside for 10 min and then evaporated to give a red oil. This was shaken with n-pentane (50 cm^3) which was then separated from the oil, and on partial evaporation afforded white crystals of $(\mathrm{Et_2NCS_2})_2$. The thiuram disulphide was recrystallised from acetone–light petroleum (b.p. 60—80 °C). The red oil was dissolved in $\mathrm{CH_2Cl_2}$ and on addition of n-hexane afforded yellow crystals of the *complex* which was filtered off and

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* Some adducts with metal dithiocarbamates and the halides of Group 5 elements have been prepared (G. Willemse, personal communication).

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recrystallised from CH_2Cl_2–n-hexane (1.3 g, 80%). The complex was also prepared using a 1 : 2 molar ratio of reactants instead of the 1 : 4 mixture reported here.

Reaction of $[Fe(S_2CNEt_2)_3][BF_4]$ *with* PPh_3.—A solution of PPh_3 (0.66 g, 2.5 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of $[Fe(S_2CNEt_2)_3][BF_4]$ (1.47 g, 2.5 mmol) in CH_2Cl_2 (30 cm^3). The reaction mixture was set aside overnight, during which time the colour had changed from brown to green. Ether was added to cause precipitation of a yellow solid which was filtered off (A), washed with ether, and recrystallised from hot ethanol. The yield of $[Ph_3P\{C(NEt_2)S\}][BF_4]$ was 0.42 g. The filtrate (A) was evaporated and the residue was dissolved in hot ethanol. After filtration, light petroleum (b.p. 120—160 °C) was added to the hot solution and Ph_3PS, which crystallised on cooling, was filtered off (B) and recrystallised from hot ethanol (0.21 g). The filtrate (B) was evaporated, and the residue was dissolved in CH_2Cl_2. Addition of n-hexane caused precipitation of unchanged $[Fe(S_2CNEt_2)_3][BF_4]$ which was filtered off; addition of ether to this filtrate caused precipitation of $[Fe(S_2CNEt_2)_3]$. This was collected and recrystallised from CH_2Cl_2–n-hexane.

Similar procedures were used to obtain the same materials (with the exception of $[Fe(S_2CNEt_2)_3][BF_4]$) from the initial reactant ratios 1.5 : 1 and 5 : 1 (PPh_3 in excess). In these cases, after long reaction times (2 days), insoluble red-brown solids of variable analyses were precipitated.

$[Fe(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2]X$; $X = BF_4$ *or* PF_6.—*Method* (a). A solution of $[Fe(S_2CNEt_2)_3][BF_4]$ (1.17 g, 2 mmol) in CH_2Cl_2 (30 cm^3) was mixed with a solution of $Ph_2PCH_2CH_2PPh_2$ (0.80 g, 2 mmol) in CH_2Cl_2 (20 cm^3) and was set aside overnight. Slow addition of ether afforded *black needles*, which were collected and washed with ether (1.0 g, 60%). This product was obtained similarly from a 1 : 2 molar reactant ratio.

Method (b). HPF_6 (60% aqueous solution, 0.23 cm^3, 1 mmol) was added to a solution of $[Fe(dppe)(S_2CNEt_2)_2]\cdot Me_2CO$ (0.81 g, 1 mmol) (see below) in $CHCl_3$ (50 cm^3). The solution turned from green to purple–black, and addition of light petroleum (b.p. 60—80 °C) afforded black crystals of the hexafluorophosphate which were filtered off and recrystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C) (0.8 g, 90%).

Method (c). $K[PF_6]$ (0.38 g) was added to a solution containing dppe (0.8 g) and $[Fe(S_2CNEt_2)_2I]$ (1.0 g) in acetone (50 cm^3). The reaction mixture was shaken vigorously for 10 min, and was then filtered to remove KI. The filtrate was evaporated to dryness and the solid hexafluorophosphate recrystallised several times from CH_2Cl_2–light petroleum (b.p. 40—60 °C) to give black crystals of the complex.

$[Co(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2][BF_4]$.—A solution of $[Co_2(S_2CNEt_2)_5][BF_4]$ (1.17 g) in CH_2Cl_2 (30 cm^3) was mixed with a solution of $Ph_2PCH_2CH_2PPh_2$ (0.80 g) in the same solvent (20 cm^3). Addition of ether caused the formation of *red crystals*, which were recrystallised from CH_2Cl_2–n-hexane (0.90 g, 53%).

$[Fe(Ph_2PCH_2CH_2PPh_2)(S_2CNEt_2)_2]\cdot Me_2CO$.—*Method* (a). This preparation was carried out under nitrogen using degassed solvents. A solution of $Na[S_2CNEt_2]\cdot 3H_2O$ (2.25 g, 1 mmol) in water (20 cm^3) was added to $FeSO_4\cdot 7H_2O$ (1.39 g, 5 mmol) in water (20 cm). The light brown precipitate which formed was filtered off and washed with acetone. A solution of $Ph_2PCH_2CH_2PPh_2$ (2.0 g, 5 mmol) in CH_2Cl_2 (40 cm^3) was added to the precipitate which immediately turned green. The green solid was extracted with CH_2Cl_2 and the resulting solution evaporated to dryness. The *complex* was recrystallised from hot acetone (3.6 g, 90%).

Method (b). A solution of $[Fe(S_2CNEt_2)_3]$ (2.0 g, 4 mmol) and $Ph_2PCH_2CH_2PPh_2$ (1.6 g, 4 mmol) in acetone (50 cm^3) was refluxed for 4 h. When the solution was cooled and filtered, green crystals were obtained (1.9 g, 62%). The filtrate was evaporated to dryness and washed with ether. Partial evaporation of the ether washings afforded white crystals of $Ph_2P(:O)CH_2CH_2P(:O)Ph_2$.

Reaction of $[Fe(S_2CNEt_2)_3][BF_4]$ *with* $PMePh_2$.—A solution of $PMePh_2$ (1.0 g) in CH_2Cl_2 (5 cm^3) was added to a solution of $[Fe(S_2CNEt_2)_3][BF_4]$ (1.5 g) in CH_2Cl_2 (30 cm^3). The mixture became dark green and was set aside for 2 h. Addition of ether caused precipitation of a solid, but attempts to separate this by fractional crystallisation using CH_2Cl_2–benzene and acetone–ether–light petroleum mixtures were unsuccessful. The filtrate, on evaporation, afforded white crystals of $P(:O)MePh_2$.

Reaction of $[Fe(S_2CNEt_2)_3]$ *with* p-ClC_6H_4NC: *Preparation of* $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$.—*Method* (a). A solution of $[Fe(S_2CNEt_2)_3]$ (5.0 g, 0.01 mol) in CH_2Cl_2 (230 cm^3) was mixed with a solution of p-ClC_6H_4NC (2.75 g, 0.02 mol) in CH_2Cl_2 (20 cm^3). After 1 h the red solution was evaporated and red crystals of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$ were obtained by slow recrystallisation of the residue from ether–n-pentane. The crystals were filtered off (A) and recrystallised from ether–n-pentane (3.4 g, 55%). White crystals of $(Et_2NCS_2)_2$ were formed upon partial evaporation of the filtrate (A). The crystals were collected, washed with n-pentane, and recrystallised from acetone–light petroleum. $[Fe(CNBu^t)_2(S_2CNEt_2)_2]$ and $[Fe(CNPr^i)_2(S_2CNEt_2)_2]$ were obtained similarly in 40% yields.

Method (b). A solution of $NaS_2CNEt_2\cdot 3H_2O$ (9.0, 0.04 mol) and p-ClC_6H_4NC (2.75 g) in degassed acetone (200 cm^3) was added to a suspension of $FeSO_4\cdot 7H_2O$ (5.6 g, 0.02 mol) in degassed acetone (100 cm^3) and the mixture was stirred rapidly under N_2 for 15 min. The solution was filtered and evaporated. The red residue was extracted with ether and addition of n-pentane to the extract caused crystallisation of the *complex*. This was collected and recrystallised from ether–n-heptane (7.5 g, 60%).

$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2][PF_6]$.—A solution of $[FeI(S_2CNEt_2)_2]$ (0.48 g, 1 mmol) and p-ClC_6H_4NC (0.27 g, 2 mmol) in CH_2Cl_2 (20 cm^3) was added to a suspension of $Tl[PF_6]$ (0.35 g, 1 mmol) in CH_2Cl_2 (20 cm^3) and the mixture was shaken overnight. The mixture was filtered and the filtrate evaporated and washed with ether. The black oil which formed was extracted with dichloromethane and on addition of n-pentane afforded crystals of the complex. Attempts to recrystallise this cation using acetone led to its reduction to $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2]$.

Reaction of $[Fe(S_2CNEt_2)_3]$ *with* CO.—$[Fe(S_2CNEt_2)_3]$ (1 g) in degassed acetone (50 cm^3) was refluxed under CO for 4 h with stirring. The i.r. spectrum of the evaporated solution showed that no reaction had apparently occurred. The solid was redissolved in acetone (50 cm^3) and stirred under CO for 3 days at room temperature. The mixture was then evaporated to dryness and extracted with ether. On evaporation, crystals of $[Fe(CO)_2(S_2CNEt_2)_2]$ were obtained.

$[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$.—A solution of $[Fe(S_2CNEt_2)_2\{CN(p\text{-}ClC_6H_4)\}_2]$ (1.24 g, 2 mmol) in acetone (50 cm^3) was added to a stirred solution of ZnI_2 (0.64 g, 2 mmol) in acetone (50 cm^3). The 1 : 1 *adduct* which precipitated was collected and recrystallised from a large volume of CH_2Cl_2 (1.61 g, 85%).

Spectrophotometric Studies of the Reactions between $[Fe(S_2CNEt_2)_3]$ *and* ZnI_2, *and between* $[FeI(S_2CNEt_2)_2]$ *and* $[Zn(S_2CNEt_2)_2]$.—Solutions of $[Fe(S_2CNEt_2)_3]$ (1×10^{-4} mol dm^{-3}), $[FeI(S_2CNEt_2)_2]$ (1×10^{-4} mol dm^{-3}), ZnI_2 (5×10^{-5} mol dm^{-3}), and $[Zn(S_2CNEt_2)_2]$ (5×10^{-5} mol dm^{-3}) were made up under nitrogen in degassed acetone. The electronic spectra of samples (1 cm^3) of solutions of ZnI_2 and $[Fe(S_2CNEt_2)_3]$ were recorded under nitrogen at 20 °C before mixing, and at intervals of 30 s, 5 min, 10 min, 3 h, and 21 h after mixing. This procedure was repeated for samples of $[FeI(S_2CNEt_2)_2]$ and $[Zn(S_2CNEt_2)_2]$. After 21 h, both mixtures, originally dark green, had become pale yellow in colour, and traces of a brown powder, (A), were visible in the bottom of the cell. These reactions were also carried out in the dark, and the spectroscopic results were similar.

Reactions between $[Fe(S_2CNEt_2)_3]$ *and* ZnI_2 *in Air.*—ZnI_2 (0.32 g, 1 mmol) was added to a solution of $[Fe(S_2CNEt_2)_3]$ (1.0 g, 2 mmol) in acetone (50 cm^3), and the reaction mixture was shaken overnight. On filtration, black crystals of $[Fe(S_2CNEt_2)_3]$ (0.21 g) were recovered, and the purple-black filtrate was evaporated to dryness *in vacuo*. The residue was crystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C), to give white crystals of $[ZnI_2(Et_2NCS_2)_2]$ (0.19 g). Evaporation of the mother liquor after removal of the zinc complex by filtration, followed by a recrystallisation of the residue, afforded a further amount of $[ZnI_2(Et_2NCS_2)_2]$ (0.09 g; total yield 45%), and a brown, uncharacterisable powder, (A).

Reaction between $[Fe(S_2CNEt_2)_3]$ *and* $ZnBr_2$ *in Air.*—This reaction was carried out in the same way as that above, using $ZnBr_2$ (0.23 g). After filtration, $[Fe(S_2CNEt_2)_3]$ (0.53 g) was obtained, and the dark green filtrate afforded, after evaporation and several recrystallisations from CH_2Cl_2–benzene mixtures, mixtures of white crystals of $[ZnBr_2(Et_2NCS_2)_2]$ and dark green $[FeBr(S_2CNEt_2)_2]$. These proved difficult to separate satisfactorily, and were identified by the i.r. spectra in KBr discs.

Reaction of $[Fe(S_2CNEt_2)_3]$ *with* $ZnCl_2$ *in Air.*—This reaction was carried out the same way as that above, affording $[Fe(S_2CNEt_2)_3]$, $[FeCl(S_2CNEt_2)_2]$, and small amounts of $[ZnCl_2(Et_2NCS_2)_2]$, the last two being identified by i.r. spectroscopy.

Reaction of $[FeI(S_2CNEt_2)_2]$ *with* $[Zn(S_2CNEt_2)_2]$ *in Air.*—$[Zn(S_2CNEt_2)_2]$ (0.36 g, 1 mmol) was added to a solution of $[FeI(S_2CNEt_2)_2]$ (0.96 g, 2 mmol) in acetone (25 cm^3) and the reaction mixture was shaken overnight. After filtration, black crystals of $[Fe(S_2CNEt_2)_3]$ (0.38 g) were obtained, and the filtrate was evaporated to dryness *in vacuo*. The grey-black residue was crystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C) to afford white crystals of $[ZnI_2(Et_2NCS_2)_2]$ and black crystals of $[Fe(S_2CNEt_2)_3]$.

Determination of the Crystal and Molecular Structure of $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$.—Deep red crystals of the compound were obtained from dichloromethane.

Crystal data. $C_{24}H_{28}Cl_2FeI_2N_4S_4Zn$, $M = 936.6$, Tetragonal, $a = 18.217(14)$, $c = 10.255(8)$ Å, $U = 3\,403(4)$ Å^3, $D_m = 1.830$, $Z = 4$, $D_c = 1.845$, $F(000) = 1\,840$. Space group $P4_12_12$ (D_4^4, No. 92) from reflection conditions $\{h00\}$, $h = 2n$, $\{00l\}$, $l = 4n$ [distinguished from enantiomeric $P4_32_12$ (D_4^8, No. 96) by anomalous dispersion results]; Mo-K_α X-radiation $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 36.7 cm^{-1}.

X-Ray data ($6.5 < 2\theta < 55°$) were collected on a Stoe Stadi-2 X-ray diffractometer from a small crystal ($0.20 \times 0.08 \times 0.04$ mm) mounted up the c axis, by the moving-crystal–stationary-counter method, with variable-width scans; background was measured at each extremity of the scan. 915 Independent reflections were obtained with $I/\sigma(I) > 3.0$ and the usual corrections were applied; no corrections were made for absorption effects. The Patterson function revealed the positions of the iodine atoms; subsequent Fourier syntheses revealed, firstly, the metal atoms lying on the crystallographic C_2 axis followed by all other non-hydrogen atoms. Block-diagonal least-squares refinement reduced R to 0.039 with allowance being made for atomic anisotropic thermal motion. Scattering factors (taken from ref. 20) were modified to allow for the anomalous scattering of metal, halogen, and sulphur atoms: no attempt was made to locate the hydrogen atoms. Unit weights were used throughout the refinement and an analysis of final structure factors did not indicate that an alternative weighting scheme would be justified.

Atomic positions with their estimated standard deviations are listed in Table 6. Observed structure amplitudes and calculated structure factors, and anisotropic thermal vibrations are listed in Supplementary Publication No. SUP 21909 (12 pp, 1 microfiche).*

TABLE 6

Positional parameters obtained from $[Fe\{CN(p\text{-}ClC_6H_4)\}_2(S_2CNEt_2)_2ZnI_2]$

Atom	X/a	Y/b	Z/c
I(1)	0.286 52(7)	0.239 56(6)	0.205 43(13)
Zn	0.313 78(19)	0.313 78(19)	0
Fe	0.445 43(23)	0.445 43(23)	0
Cl(1)	0.903 4(2)	0.539 6(3)	−0.208 3(6)
S(1)	0.318 3(2)	0.443 5(2)	0.051 1(4)
S(2)	0.387 0(2)	0.482 3(2)	−0.188 3(5)
C(1)	0.305 2(9)	0.475 7(7)	−0.108 8(17)
N(1)	0.239 8(7)	0.490 5(7)	−0.159 5(13)
C(2)	0.171 9(9)	0.476 5(10)	−0.082 8(19)
C(3)	0.123 3(12)	0.541 9(11)	−0.075 7(25)
C(4)	0.233 1(10)	0.518 2(10)	−0.297 0(15)
C(5)	0.249 7(12)	0.602 1(10)	−0.305 4(19)
C(6)	0.539 6(9)	0.455 0(8)	−0.060 4(18)
N(2)	0.599 5(7)	0.461 5(9)	−0.094 0(15)
C(7)	0.670 4(8)	0.477 9(8)	−0.125 6(18)
C(8)	0.693 7(9)	0.553 0(9)	−0.113 1(16)
C(9)	0.765 4(8)	0.572 1(9)	−0.136 0(16)
C(10)	0.813 3(8)	0.517 4(10)	−0.175 4(18)
C(11)	0.791 8(10)	0.443 0(10)	−0.187 8(20)
C(12)	0.717 0(10)	0.425 1(9)	−0.159 5(19)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[20] 'International Tables for X-Ray Crystallography,' vol. 4, 1974, Kynoch Press, Birmingham.