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3-Ferrocene-substituted 3-mercaptopropenales and their Schiff bases as ligands for transition metal complexes [1]

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Abstract

Nucleophilic substitution of chlorine by sulphur in 3-ferrocenyl-3-chloropropenale and 1,1′-bis(3-chloropropenale)ferrocene yields the air-sensitive 3-ferrocenyl-3-mercaptopropenale and the 1,1′-bis(3-mercaptopropenale)ferrocene, respectively. These compounds form stable neutral chelates with zinc(II), nickel(II), cobalt(II) and copper(II). Their Schiff bases with aniline or primary diamines, obtained by direct reaction of the free 3-ferrocene-substituted 3-mercaptopropenales or by reaction with their transition metal chelates, are excellent ligands for electron-rich transition metals. The X-ray structure determination of bis(β-ferrocenyl-β-mercapto-*N*-phenyl-vinylaldiminato)nickel(II) indicates S,O coordination and *cis* arrangement of the ligands. The coordination sphere is distorted tetrahedrally. Cyclic voltammetry reveals only a slight influence of the bound transition metal on the electron density within the ferrocene subunit. © 1998 Elsevier Science S.A.

Keywords: Ferrocene complexes; Schiff base complexes; Crystal structures; Trinuclear complexes

1. Introduction

Coordination compounds of transition metal ions containing the redox-active ferrocene moiety have been investigated intensively in recent years [1].

In this context efforts are aimed towards the synthesis of molecules that allow interactions between the ferrocene iron and additional metal ions bound at side chains of the cyclopentadienyl rings. Therefore, close proximity of the two metal ions [2–4] and/or a conjugated pathway between the metals [5–7] is desired.

These requirements are met by ferrocene-substituted 1,3-bischalcogenates [ferrocene-CX-Y-CZ-R with X, Z = O, S, (Se); Y = CH_2, NH]. Considering the additional merit of a rich, well-understood coordination chemistry of these compounds, they should be a favoured object of investigation.

Except for some early work by Weinmayr [8] and Wolf, Hennig and coworkers [9] on ferrocenoyl acetone (X, Z = O; Y = CH_2), there are no publications relating to this class of compounds.

We extended the idea of ferrocene-substituted 1,3-bischalcogenates to the coordinatively rich *N*,*N*-disubstituted *N*′-ferrocenoyl thioureas (X = O; Y = NH; Z = S; R = NR_2) [10]. Cyclic voltammetric studies revealed a distinct change in electron density upon complexation [11].

Another approach to ferrocenyl-substituted ligands is given by 3-ferrocenyl-3-mercaptopropenale and its respective 1,1′-disubstituted ferrocene derivative, which is presented in this study (tautomeric form of X = S; Y = CH_2; Z = O; R = H). Compared with the *N*,*N*-disubstituted *N*′-acylthioureas mentioned above, β-mercaptovinylaldehydes are excellent ligands for electron-rich transition metal ions. In addition, they allow further modifications by reactions with primary amines [12]. Starting with 3-ferrocenyl-substituted 3-chloropropenale (a widely used precursor for ferrocenylalkines [13]), a variety of ligand systems and their chelates can be obtained.

2. Experimental

All chemicals and solvents were dried and purified by the usual methods. Melting points are corrected and were measured using a Boëtius melting-point apparatus. Mass spectra were recorded on a Masslab VG 12-250 device. IR spectra were measured with a Specord M80 by Carl Zeiss Jena (KBr-pellets). NMR spectra ($CDCl_3$) were recorded on a Varian Gemini (200 MHz) spectrometer with tetramethylsilane as internal standard.

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[1] Dedicated to Professor Horst Hennig on the occasion of his 60th birthday.

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2.1. Preparation of the compounds

2.1.1. 3-Ferrocenyl-3-mercaptopropenale **1** [2]

$Na_2S \cdot 9H_2O$ (1.32 g, 0.0055 mol) was dissolved in methanol (50 ml) under an Ar atmosphere. 3-Ferrocenyl-3-chloropropenale [14] (1 g, 0.0036 mol) was added slowly in small portions. After 2 h of stirring at room temperature, Ar-saturated water (50 ml) was added, followed by extraction with ether (20 ml, three times). Methylene chloride (30 ml) was added to the aqueous layer and the solution was acidified with 1 M aqueous HCl. The mixture was stirred for another 30 min. The dark violet organic layer was separated from the blue aqueous phase and washed with Ar-saturated water until neutral.

2.1.2. 1,1′-Bis(3-mercaptopropenale)ferrocene **2** [3]

Same procedure as for **1**, using 0.0084 mol (2.00 g) $Na_2S \cdot 9H_2O$ and 0.00276 mol (1 g) 1,1′-bis(3-chloropropenale)ferrocene [13b].

Analytical data of the following compounds are summarized in Table 1.

2.1.3. Transition metal complexes of 3-ferrocenyl-3-mercaptopropenale with: zinc(II) ***1a****, cobalt(II)* ***1b****, nickel(II)* ***1c****, copper(II)* ***1d***

A solution of the respective metal acetate (0.0018 mol, 0.40 g $Zn(ac)_2 \cdot 2H_2O$; 0.45 g $Co(ac)_2 \cdot 4H_2O$; 0.42 g $Ni(ac)_2 \cdot 4H_2O$; 0.36 g $Cu(ac)_2 \cdot H_2O$) dissolved in methanol (50 ml) was slowly added to a vigorously stirred solution of **1** under an Ar atmosphere. After three hours of stirring at room temperature, the solvent was removed and the air-stable products were recrystallized from methanol/methylene chloride (2:1).

Yields (calculated for 3-ferrocenyl-3-chloropropenale): **1a**: 83% (0.91 g); **1b**: 70% (0.76 g); **1c**: 80% (0.86 g); **1d**: 87% (0.95 g).

2.1.4. Transition metal complexes of 1,1′-bis(3-mercaptopropenale)ferrocene with: zinc(II) ***2a****, cobalt(II)* ***2b***

A solution of 0.0028 mol of the respective metal acetate (0.61 g $Zn(ac)_2 \cdot 2H_2O$, 0.69 g $Co(ac)_2 \cdot 2H_2O$) in 80 ml methanol was added to **2** following the procedure outlined above.

Yields (calculated for 1,1′-bis(3-chloropropenale)-ferrocene): **2a**: 70% (0.81 g); **2b**: 75% (0.86 g).

2.1.5. Schiff bases of 3-ferrocenyl-3-mercaptopropenale ***1*** *with: aniline* ***3****, ethylenediamine* ***4****, di(4-anilino)methane* ***5***

(a) A solution of 0.0036 mol (0.34 g) freshly distilled aniline or 0.0018 mol of the respective diamine (0.11 g ethylenediamine; 0.36 g di(4-anilino)methane) in 50 ml methanol was added to a methylene chloride solution of **1** (obtained according to Section 2.1.1.) under argon at room temperature. The colour changed to brown immediately. After one hour of stirring the product was extracted with methylene chloride, washed twice with 50 ml 1 M HCl and three times with 50 ml water. The solvent was removed and the product was recrystallized from methanol/methylene chloride (3:1).

Yields (calculated for 3-ferrocenyl-3-chloropropenale): **3**: 68% (0.85 g); **4**: 60% (0.61 g); **5**: 65% (0.83 g).

(b) A solution of 0.0036 mol (0.34 g) freshly distilled aniline or 0.0018 mol of the respective diamine (0.11 g ethylenediamine; 0.36 g di(4-anilino)methane) in 30 ml ethanol was added to an ethanol suspension of 0.0018 mol **1a** (1.1 g in 50 ml). The mixture was stirred for 24 h at room temperature. After the addition of 80 ml water, the working up of (a) resulted in the following yields (calculated for **1a**): **3**: 89% (1.11 g); **4**: 85% (0.87 g); **5**: 85% (1.1 g).

2.1.6. Dianile of 1,1′-bis(3-mercaptopropenale)ferrocene **6**

The procedures (a) and (b) of Section 2.1.5. can be employed as well:

(a) using 0.0055 mol (0.51 g) aniline and the methylene chloride solution of **2** (obtained according to Section 2.1.2.),

(b) mixing 0.0055 mol (0.51 g) aniline with 0.0028 mol (1.16 g) **2a** in methylene chloride.

Yields of **6**: (a) 60% (0.84 g); (b) 78% (1.1 g).

2.1.7. Transition metal chelates of the Schiff bases ***3****,* ***4****,* ***5****,* ***6*** *with: zinc(II)* ***3a****,* ***4a****,* ***5a****,* ***6a****; cobalt(II)* ***3b*** *and nickel(II)* ***3c****,* ***5c***

(a) Substance **3** (0.14 g, 0.0004 mol) or **4** (0.11 g, 0.0002 mol) or **5** (0.14 g) or **6** (0.10 g) was dissolved in 30 ml methylene chloride. A solution of 0.0002 mol of the respective metal acetate (0.044 g $Zn(ac)_2 \cdot 2H_2O$; 0.050 g $Co(ac)_2 \cdot 2H_2O$; 0.047 g $Ni(ac)_2 \cdot 2H_2O$) in methanol (50 ml) was added. The mixture was allowed to stir for five hours at room temperature. After removal of the solvent, products were purified by recrystallization from methanol/methylene chloride (1:1).

Yields (calculated for the ligands): **3a** 75% (0.11 g), **3b** 80% (0.12 g), **3c** 68% (0.10 g), **4a** 70% (0.09 g), **5a** 77% (0.12 g), **5c** 60% (0.09 g), **6a** 86% (0.09 g).

(b) Chelates **3a**, **3b**, **3c** are also accessible following the slightly modified procedure (b) of Section 2.1.5.: starting with 0.0002 mol (0.12 g) **1a**, **1b** or **1c** and 0.0004 mol aniline (0.04 g), the desired coordination compounds can be obtained following this procedure but omitting treatment with HCl solution.

Yields (calculated for **1a**, **1b**, **1c**): **3a** 70% (0.11 g), **3b** 65% (0.10 g), **3c** 70% (0.11 g).

2.2. X-ray structure determination of ***3c***

A dark-brown plate (0.27 mm × 0.19 mm × 0.10 mm) of **3c** was mounted on a Stoe Stadi 4 diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation

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[2] **1** and **2** are not stable under atmospheric conditions. Solutions of **1** and **2** in methylene chloride were used for further reactions without isolation of the ferrocene derivatives.

[3] See footnote 2.

Table 1
Analytical data

Compound	m.p. (°C)	C calc./found	H	N	O	S	MS (% rel. int.) F.A.B. or 70 eV	^{1}H-NMR (ppm) CDCl$_3$	^{13}C-NMR (ppm) CDCl$_3$	IR (KBr)
1a	104 (dec.)	51.41 51.40	3.65 3.80		5.27 5.93	10.54 10.21	F.A.B. 607(M^+, 43), 271(lig.$^+$, 30), 229(FeCS, 100)	4.20(s,10H,Cp′), 4.60(s,4H,Cp3,4), 5.00(s,4H,Cp2,5), 6.55(d,J = 3.2 Hz,2H,CH), 8.64(d,J = 3.2 Hz,2H,CHO)	70.11(Cp2,5), 71.96 (Cp′), 73.15(Cp3,4), 87.83(Cpq), 114.77 (CH), 184.76(CS), 192.10(CO)	1639(s), 1563(m), 1480(s, CO), 1374(s)
1b	232 (dec.)	51.96 51.58	3.69 3.60		5.32 5.22	10.65 10.10	F.A.B. 601(M^+, 90), 271(lig.$^+$, 85), 213(FeCO, 100)			1637(br, 1562(m), 1468(s, CO), 1376(s)
1c	117–120 (dec.)	51.96 52.30	3.69 4.08		5.32 5.41	10.65 10.48	F.A.B. 600(M^+, 5), 329(lig. + Ni, 30), 307(100)	4.20(s,10H,Cp′), 4.55(s,4H,Cp3,4), 4.88(s,4H,Cp2,5), 6.56(d,J = 3.3 Hz,2H,CH), 7.86(d,J = 3.3 Hz,2H,CHO)	69.48(Cp2,5), 71.83 (Cp′), 72.71(Cp3,4), 83.28(Cpq), 113.5 (CH), 147.9(CO), 177.42(CS)	1635(br), 1542(m), 1473(s, CO), 1377(s)
1d	225–228 (dec.)	51.56 51.83	3.66 4.01		5.28 5.33	10.57 10.70	F.A.B. 605(M^+, 9), 480(100), 271(lig.$^+$, 10)			1651(br), 1556(m), 1480(s, CO), 1377(m), 1361(m)
2a	>220 (dec.)	45.66 45.32	2.87 3.08		7.59 7.92	15.19 15.41	F.A.B. 422(MH^+, 23), 395(40), 229(FeCS, 100)	4.57(s,4H,Cp3,4), 4.97(s,4H,Cp2,5), 6.49(d,J = 3.4 Hz,2H,CH), 8.69(d,J = 3.4 Hz,2H,CHO)	70.00(Cp2,5), 73.21 (Cp3,4), 86.56(Cpq), 114.55(CH), 185.30 (CS), 191.86(CO)	1610(br), 1567(s), 1477(s), 1375(s)
2b	>210 (dec.)	46.41 46.78	2.92 2.95		7.73 7.42	15.46 15.38	F.A.B. 414(M^+, 25), 327(lig-(CHC), 58) 282(lig-(FeCpC),100)			1647(br), 1583(m), 1467(s, CO), 1376(m)
3	164	65.72 65.31	4.94 4.68	4.03 4.42		9.22 9.58	347(M^+, 100), 313(M-(H_2S), 10), 194(PhNCHCHCCp, 40), 77(Ph, 40)	4.13(s,5H,Cp′), 4.55(s, 2H,Cp3,4), 4.98(s,2H,Cp2,5), 6.44(d,J = 4 Hz,1H,CH), 7.19(m,3H,Ph), 7.35(m,2H,Ph), 7.62(m,1H,CHN), 14.8(br,1H,NH)	69.79(Cp2,5), 71.55 (Cp′), 72.80(Cp3,4), 90.90(cpq), 108.63(CH), 117.91 (oPh), 125.12(pPh), 130.37(mPh), 140.38 (qPh), 143.70(CHN), 213(CS)	1620(s, CN) 1583(s), 1489(s), 1309(s), 1260(s)
3a	217	60.26 60.52	4.26 4.38	3.70 3.61		8.45 8.47	F.A.B. 757(M^+, 50), 572(M-(Fc), 100)	4.18(s,10H,Cp′), 4.45(s,4H,Cp3,4), 4.90(s,2H,Cp), 4.98(s,2H,Cp), 6.45(d,J = 7.1 Hz,2H,CH) 7.11(m,6H,Ph) 7.25(m,4H,Ph) 7.67(d,J = 7.1 Hz,2H,CHN)	68.81(Cp), 70.04 (Cp), 71.34(Cp′), 71.50(Cp), 71.59 (Cp), 89.73(Cpq), 112.68(CH), 126.55 (oPh), 128.36(pPh), 131.95(mPh), 146.01(qPh), 158.91 (CHN), 177.67(CS)	1623(br), 1501(s, CN), 1482(s), 1371(s)

3b	197	60.77 61.02	4.29 4.18	3.73 3.54	8.52 8.13	F.A.B. 752(M+H⁺, 100)			1625(br), 1496(s), 1479(s), 1362(s)
3c	241	60.77 60.83	4.29 4.30	3.73 3.48	8.52 8.21	F.A.B. 751(M⁺, 10), 347(lig+H⁺, 100)	4.24(s,10H,Cp′), 4.52(s,4H,Cp3,4), 5.00(s,4H,Cp2,5), 6.73(d,J=7.1 Hz,2H,CH), 7.28–7.32(m,10H,Ph), 7.53(d,J=7.1,2H,CHN)	70.59(Cp2,5), 77.35 (Cp′), 71.53(Cp3,4), 90.00(Cpq), 111.97 (CH), 122.68 (oPh), 126.55(pPh), 128.36(mPh), 151.58(qPh), 158.91 (CHN), 178.91(CS)	1623(br), 1497(s) 1479(s), 1363(s)
4	> 199 (dec.)	59.20 58.88	4.97 5.21	4.93 5.39	11.27 11.04	568(M⁺, 5), 503 (M-(Cp),15), 122 (FeCp, 45), 66(H$_2$S$_2$, 100)	3.55(m,4H,CH$_2$), 4.12(s,10H,Cp′), 4.49(pt,J=1.9 Hz,4H, Cp3,4), 4.91(pt,J=1.9 Hz,4H, Cp2,5), 6.25(d,J=7.8 Hz,2H,CH) 7.07(dd,J1=7.8 Hz,J2= 12.8Hz,2H,CHN), 13.25(d,J=13 Hz,2H,NH)	50.74(CH$_2$),70.32 (cp2,5), 71.42(Cp′), 72.35(Cp3,4), 90.41 (Fcq), 107.46(CH), 154.00(CHN), 210 (CS)	1623(s, CN), 1496(s), 1267(m)
4a	190(dec.)	53.26 53.01	4.15 4.42	4.43 4.78	10.14 10.09	F.A.B. 631.1(M⁺, 25), 567(lig-(H), 82), 269(FcCSCHCHN, 100)	3.49(m,4H,CH$_2$), 4.26(s,10H,Cp′), 4.49(s,4H,Cp3,4), 4.89(s,4H,Cp2,5), 6.48(d,J=6.9 Hz,2H,CH), 7.68(d,J=7 Hz,2H,CHN)	50.9(CH$_2$), 69.58 (Cp2,5), 71.40(Cp′), 71.58(Cp3,4), 90.08(Fcp), 111.83 (CH), 160.8(CHN), 177.58(CS)	1618(br), 1506(s), 1407(m)
5	> 120 (dec.)	66.34 66.18	5.14 5.12	3.97 3.92	9.06 9.16	F.A.B. 706(M⁺, 15), 452(100)	3.93(s,2H,CH$_2$), 4.15(s,10H,Cp′), 4.55(s,4H,Cp3,4), 4.98(s,4H,Cp2,5), 6.44(br,2H,CH), 7.15(br,8H,Ph), 7.60(m,2H,CHN), 14.86(br.,2H,NH)	41.50(CH$_2$), 69.75 (Cp2,5), 71.52(Cp′), 72.73(Cp3,4), 90.5(Cpq), 101.3(CH), 118.15 (Ph), 130.79(Ph), 136.83(qPh), 143.07 (qPh), 143.98 (CHN), 209.72(CS)	1621(s,CN), 1579 (s), 1485(s), 1307 (s), 1260(s)
5a	> 360	60.79 60.21	4.19 4.21	3.63 3.6	8.31 8.27	F.A.B. 1541.5(M⁺, 100)	3.83(s,4H,CH$_2$),2 4.26(s,20H,Cp′), 4.49(pt,J=2 Hz,8H,Cp3,4), 5.00(pt,J=2 Hz,8H,Cp2,5), 6.50(d,J=7 Hz,4H,CH), 6.81, 6.85, 6.92, 6.96(s, 16H,Ph), 7.66(d,J=7 Hz,4H,CHN)	40.41 (CH$_2$), 68.72(Cp), 70.21(Cp), 71.39 (Cp′), 71.52(Cp), 71.62(Cp), 89.52 (Cpq), 112.12(CH), 122.4(Ph), 129.98(Ph), 138.76 (qPh), 149.26(qPh), 161.38(CHN), 177.11(CS)	1622(br), 1490(s), 1373(m)

(continued)

Table 1 (*continued*)

Compound	m.p. (°C)	C calc./found	H	N	O	S	MS (% rel. int.) F.A.B. or 70 eV	^{1}H-NMR (ppm) $CDCl_3$	^{13}C-NMR (ppm) $CDCl_3$	IR (KBr)
5c	170–174 (dec.)	61.41 61.10	4.29 4.28	3.67 3.85		8.39 8.56	F.A.B. 1527(M+2H$^+$, 100%)	3.30(s,4H,CH_2), 4.25(s,20H,Cp′), 4.51(s,8H,Cp3,4), 5.02(s,8H,Cp2,5), 6.95(br,4H,CH), 7.10(br,16H,Ph), 7.51(br,4H,CHN)		1609(br), 1487(s), 1416(m), 1361(m)
6	115–120 (dec.)	66.20 66.15	4.76 4.91	5.51 5.76		12.59 12.90	508(M$^+$, 10), 474(M−(H_2S), 20), 93($PhNH_2^+$, 100)	4.53(s,4H,Cp3,4), 4.91(s,4H,Cp2,5), 6.41/d,J = 7.8 Hz,2H,CH), 7.17, 7.37(m,10H, Ph), 7.56(m,2H,CHN), 14.83(d,J = 13.4 Hz,2H, NH)	71.83(Cp2,5), 75.04(Cp3,4), 92.96 (Cpq), 110.29(CH), 118.08(oPh), 125.28 (pPh), 130.42(mPh), 140.29(qPh), 144.08 (CHN), 212.17(CS)	1622(s, CN), 1583 (s), 1483(s), 1309(s), 1259(m)
6a (polymer)	>200 (dec.)	58.89 59.00	3.88 4.22	4.90 4.95		11.21 11.17				1623(br), 1500(s, CN), 1482(s), 1373(m)

Table 2
Crystallographic data for **3c**

Molecular formula	$C_{38}H_{32}Fe_2N_2NiS_2$
Formula weight	751.19
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	10.161(1)
b (Å)	12.739(2)
c (Å)	25.302(3)
Volume (Å^3)	3275.1(7)
Z	4
Density (calc.) (g cm^{-3})	1.523
Absorption coefficient (mm^{-1})	1.601
F(000)	1544

(λ=0.71069 Å). Details of crystal data are summarized in Table 2.

A total of 8580 reflections were collected at room temperature (ω–θ scan method, 2θ range 3–55°). Of the unique 7660 reflections, only 2722 were observed ($I>2\sigma(I)$). Lorentz-polarization corrections and absorption corrections by psi scans were applied to the intensity data.

The structure was solved by Patterson methods (SHELXS-86 [15]) and the non-hydrogen atoms were refined anisotropically (SHELXL-93 [16]). In the final cycle of least-squares refinement 406 variable parameters were refined on the basis of 7659 reflections. The positions of all hydrogen atoms were calculated and included with isotropic temperature factors 1.2 times higher than U_{eq} of the parent C atoms.

The final R values were R_1=0.0565 for 2722 observed reflections and wR_2=0.1185 for 7659 unique reflections. The Flack parameter was −0.03(3).

The maximum and minimum difference peaks were 0.42 and −0.51 e Å^{-3}. The final atomic coordinates for the non-hydrogen atoms and selected distances and angles are given in Tables 3 and 4, respectively.

Table 3
Atomic coordinates and equivalent isotropic thermal parameters for **3c**

Atom	x	y	z	U_{eq} (Å^2) ^{a}
Ni1	0.1419(1)	0.0902(1)	0.9074(1)	0.0333(3)
Fe1	0.5743(1)	−0.1653(1)	0.8233(1)	0.0432(4)
Fe2	−0.0061(1)	0.4764(1)	0.8093(1)	0.0451(4)
S1	0.3191(2)	0.0546(2)	0.8648(1)	0.0455(7)
S2	0.1057(2)	0.1906(2)	0.8406(1)	0.0531(8)
N1	0.2101(7)	0.0602(5)	0.9762(2)	0.036(2)
N2	−0.0402(7)	0.0707(5)	0.9260(2)	0.039(2)
C1	0.4333(8)	−0.0089(6)	0.9028(3)	0.037(2)
C2	0.4197(8)	−0.0224(6)	0.9558(3)	0.038(2)
C3	0.3212(9)	0.0147(7)	0.9894(3)	0.041(2)
C4	0.5518(8)	−0.0433(7)	0.8755(3)	0.038(2)
C5	0.5958(9)	−0.0065(7)	0.8245(4)	0.061(3)
C6	0.7180(10)	−0.0543(8)	0.8131(4)	0.070(3)
C7	0.7492(10)	−0.1215(9)	0.8554(4)	0.067(4)
C8	0.6496(10)	−0.1164(7)	0.8929(4)	0.055(3)
C9	0.3945(11)	−0.2238(10)	0.8042(6)	0.084(4)

(*continued*)

Table 3 (*continued*)

Atom	x	y	z	U_{eq} (Å^2) [a]
C10	0.4697(16)	−0.2083(11)	0.7590(5)	0.094(4)
C11	0.5817(12)	−0.2658(11)	0.7614(5)	0.082(4)
C12	0.5807(13)	−0.3226(9)	0.8085(5)	0.080(3)
C13	0.4659(14)	−0.2973(9)	0.8356(5)	0.078(4)
C14	0.1331(8)	0.0962(7)	1.0199(3)	0.036(2)
C15	0.1069(8)	0.0367(7)	1.0638(3)	0.042(2)
C16	0.0284(9)	0.0753(8)	1.1044(3)	0.048(3)
C17	−0.0198(11)	0.1737(8)	1.1018(4)	0.063(3)
C18	0.0061(11)	0.2345(7)	1.0585(4)	0.067(3)
C19	0.0826(9)	0.1998(7)	1.0183(3)	0.050(3)
C20	−0.0496(8)	0.2422(6)	0.8431(3)	0.039(2)
C21	−0.1463(10)	0.2097(7)	0.8765(4)	0.054(3)
C22	−0.1434(9)	0.1238(6)	0.9102(3)	0.048(2)
C23	−0.0737(8)	0.3261(7)	0.8033(3)	0.038(2)
C24	0.0055(10)	0.3517(7)	0.7592(3)	0.041(2)
C25	−0.0521(9)	0.4384(7)	0.7329(3)	0.047(3)
C26	−0.1647(10)	0.4689(7)	0.7601(3)	0.054(3)
C27	−0.1803(8)	0.4009(7)	0.8043(3)	0.050(2)
C28	0.0831(25)	0.4862(14)	0.8808(6)	0.148(10)
C29	0.1742(16)	0.5028(14)	0.8400(9)	0.135(8)
C30	0.1322(17)	0.5876(13)	0.8102(6)	0.113(5)
C31	0.0202(16)	0.6280(8)	0.8333(5)	0.090(4)
C32	−0.0078(16)	0.5658(11)	0.8749(5)	0.099(5)
C33	−0.0687(8)	−0.0207(6)	0.9580(3)	0.030(2)
C34	−0.1626(9)	−0.0178(8)	0.9980(3)	0.047(3)
C35	−0.1897(9)	−0.1078(8)	1.0264(3)	0.050(3)
C36	−0.1245(11)	−0.2004(8)	1.0154(4)	0.065(3)
C37	−0.0285(11)	−0.2043(8)	0.9757(4)	0.061(3)
C38	−0.0050(10)	−0.1140(7)	0.9464(3)	0.044(2)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 4
Selected distances (Å) and angles (°) for **3e**

Ni1–S1	2.147(3)	Ni1–S2	2.152(2)
Ni1–N1	1.912(7)	Ni1–N2	1.925(7)
S1–C1	1.711(8)	S2–C20	1.711(9)
N1–C3	1.313(10)	N2–C22	1.310(10)
N1–C14	1.429(9)	N2–C33	1.449(9)
C1–C2	1.359(10)	C20–C21	1.360(11)
C1–C4	1.456(10)	C20–C23	1.489(11)
C2–C3	1.394(10)	C21–C22	1.388(11)
Fe1–C_{cp} (mean)	2.034	Fe2–C_{cp} (mean)	2.028
C_{cp}–C_{cp} (mean)	1.401		
S1–Ni1–N1	96.4(2)	S2–Ni1–N2	96.0(2)
Ni1–S1–C1	112.7(3)	Ni1–S2–C20	110.8(3)
Ni1–N1–C3	129.2(6)	Ni1–N2–C22	129.0(6)
Ni1–N1–C14	116.2(5)	Ni1–N2–C33	115.6(6)
C3–N1–C14	114.6(7)	C22–N2–C33	115.2(7)
S1–C1–C2	123.1(7)	S2–C20–C21	125.0(7)
C1–C2–C3	129.1(8)	C20–C21–C22	127.3(10)
N1–C3–C2	127.8(8)	N2–C22–C21	127.7(9)

2.3. *Cyclic voltammetry*

Cyclic voltammetry was performed using a conventional three-electrode system. The working electrode was a glassy carbon disc (Metrohm, number: 6.1204.000, ∅ = 3 mm), polished with an Al_2O_3 suspension prior to every experiment. The counter electrode was a platinium disc (Sensortechnik, Meinsberg, Germany). A double-junction Ag/AgCl electrode was used as reference (Metrohm, number: 6.0726.110). The inner chamber was filled with a saturated solution of LiCl in ethanol and the outer chamber contained a 0.1 M Bu_4NClO_4 (TBAPC) solution in methylene chloride. Methylene chloride was of p.a. grade and saturated with nitrogen. The concentration of supporting electrolyte TBAPC was 0.1 M. The concentration of compounds investigated was 1 mM.

The estimated error of the measured voltage is about 0.01 V. All data represent the average of three measurements.

Voltammograms were recorded with the electrochemical interface (SI 1280, Solartron-Schlumberger) under application of the software CORRWARE (Scribner, Charlottesville, VA).

3. Results and discussion

3.1. *Synthesis*

Starting with 3-ferrocene-substituted 3-chloropropenales, the air-sensitive title compounds are obtained by nucleophilic substitution of chlorine by sulphur using NaS^- and subsequent acidic work-up.

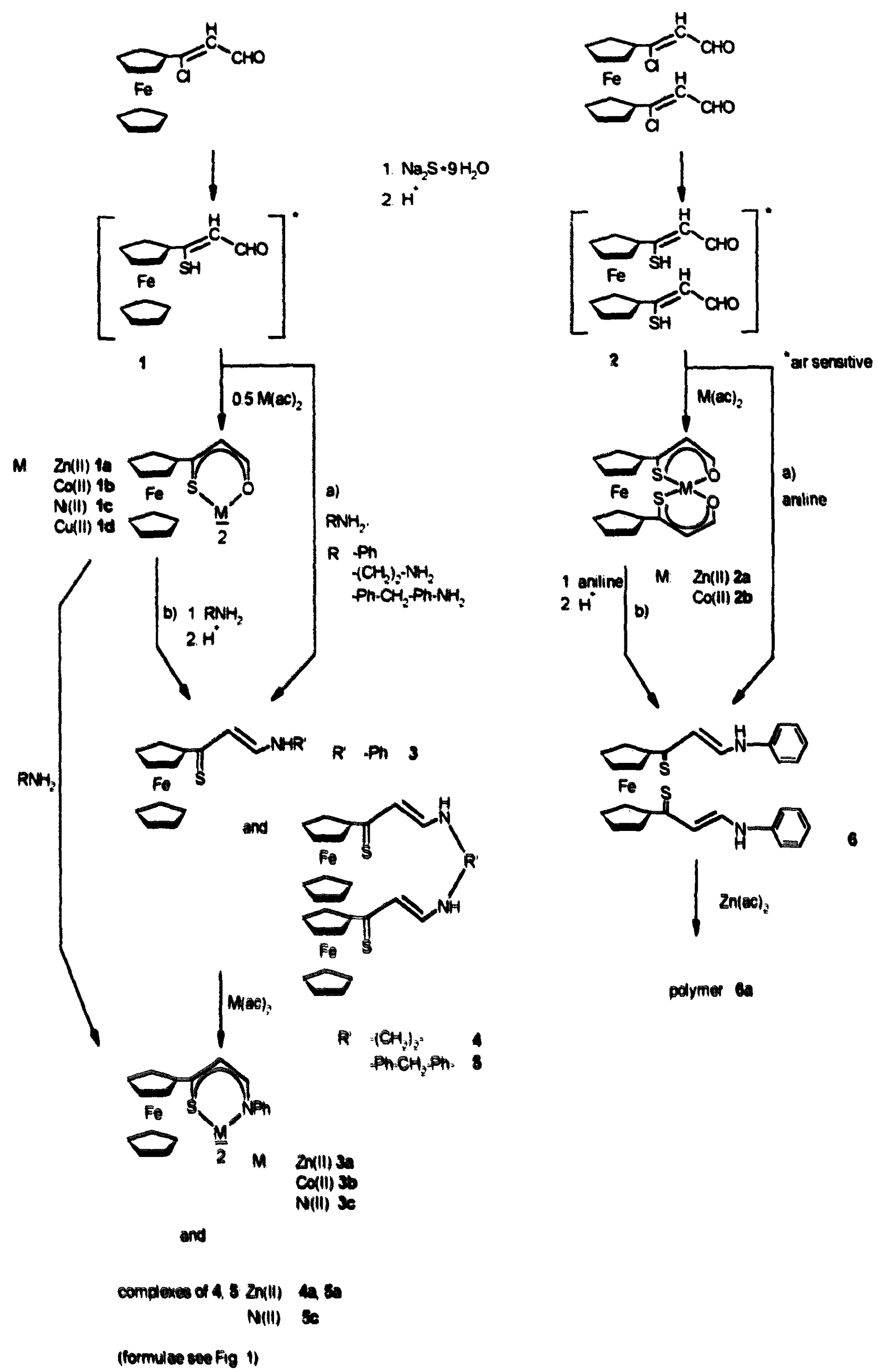
On the one hand they are stabilized by transition metal ions (Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) yielding neutral 2:1 O-, S- chelates. As indicated by all IR and NMR spectra of **1a** and **1c** (Table 1), coordination onto the carbonyl oxygen is more pronounced in the Ni- and Co- chelates. For example, the 44 ppm shift difference between the aldehyde ^{13}C-NMR signals of **1a** and **1c** shows much stronger metal–oxygen bonding in the nickel chelate.

1,1′-Bis(3-mercaptopropenale)ferrocene **2** does not show any tendency to form polymer complexes with Zn^{2+} or Co^{2+}.

The coordination compounds **1a–d** and **2a–b** are appropriate storage forms of **1** and **2** because the metal is easily removed by treatment with acid. Furthermore, reactions at the coordinated ligands are possible. Addition of primary amines gives the respective Schiff bases **3–6** (acidic work-up) or their transition metal chelates (neutral work-up) in high yields.

On the other hand, direct reaction of **1** and **2** with amines results in the air-stable Schiff bases **3–6** as well. The analytical data give evidence that the compounds occur in the NH-tautomeric form like enamine thioketones. This can be deduced from the low-field-shifted ^{1}H-NMR doublet of the NH proton. Nevertheless, yields are lower than when employing chelates **1a** or **2a**. Obviously, the free thioketo group of **1** and **2** is also partially attacked by amine.

Compounds **3–6** yield S- and N- coordinated bis-chelates with Zn^{2+}, Co^{2+} and Ni^{2+}. This could be proved by X-ray



Scheme 1.

structure investigation of the nickel chelate **3c**. Scheme 1 summarizes the reaction pathways.

As revealed by FAB-MS, the bridged Schiff bases **4** and **5** exhibit different coordination behaviour. The flexible ethylene bridge allows the formation of a ligand:metal = 1:1 Zn-chelate **4a** while **5**, with its more rigid bridge, gives 2:2 Zn- and Ni-compounds **5a**, **5c** (Fig. 1).

Reaction of the dianile **6** with zinc acetate only results in the respective polymer **6a**.

3.2. X-ray structure of 3c

The molecular structure of **3c** is shown in Fig. 2. The complex molecule is a bis-chelate with a tetrahedrally distorted square-planar coordination of the S and N atoms. The coordination angle between the planes Ni1/S1/N1 and Ni1/S2/N2 is 33.9(2)°. The arrangement of the ligator atoms is cis with an interligand S–S distance of 2.842(3) Å.

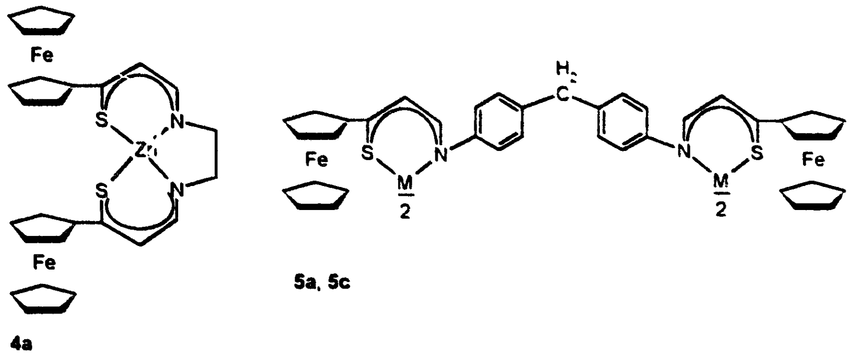


Fig. 1. Different coordination behaviour of chelates **4a** and **5a**/**5c**.

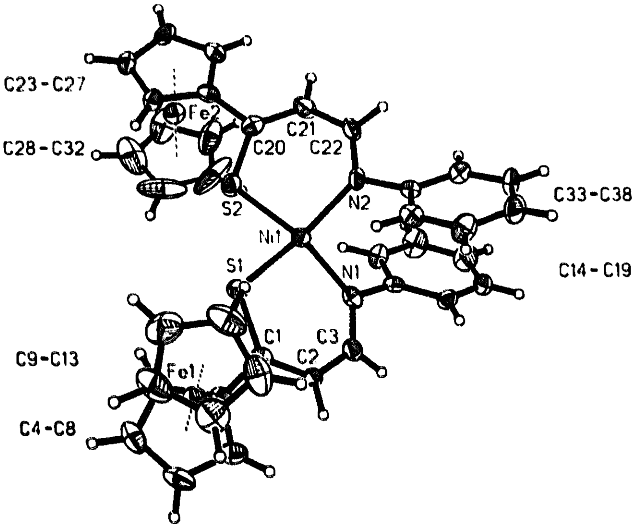


Fig. 2. Molecular structure of **3c**.

All bond lengths in the chelate rings are between single and double bonds. This result suggests a π-electron delocalization in the chelate rings.

The substituted cyclopentadienyl rings of the ferrocene units form angles with the chelate rings of 18 and 16°. The cyclopentadienyl rings are parallel in both units and deviate from an eclipsed conformation by 17.1 and 7.5°. The phenyl rings are nearly parallel with a dihedral angle between the ring planes of 14°. They form angles with the attached chelate rings of 46 and 43°.

3.3. *Cyclic voltammetric studies*

Cyclic voltammetry within the potential range 0 to + 1.2 V of chelates **1a–d** and **2a–b** reveals one quasi-reversible redox couple, assigned to Fe(II)/Fe(III); a ferrocene–ferrocene interaction can therefore be excluded. Repeated potential cycling results in increasing currents, indicating compound deposition on the electrode surface.

Cyclic voltammograms (CVs) of **3**, **4**, **5** and of their chelates are more complex. Fig. 3 displays the CV of **5a** as a representative example. The ferrocene-centred oxidation (A) at a potential of about 0.6 V is followed by a redox process (B) at about 0.8–0.9 V. It is amine dependent and also occurs at ferrocene-free enamine beta-thioketones, as comparative measurements on Schiff bases of 3-mercapto-3-(4-methoxyphenyl)propenale with various substituted anilines revealed, and should therefore be attributed to the enamine function. Redox process (B) is shifted anodically by 50–60 mV upon coordination. In the free ligands **3–5** oxidation (A) is irreversible. Coordination reveals a corresponding reduction. CVs of **6** and **6a** do not show a separation of processes (A) and (B). Therefore, no data could be obtained for these compounds.

The data of ferrocene-centred redox processes are presented in Table 5.

As expected, substitution of chlorine by sulphur in the 3-ferrocene-substituted 3-chloropropenales leads to a less emphasized anodic shift of the Fe(II)/Fe(III) redox couple of **1a–d**, **2a–b** compared with ferrocene as internal standard. The magnitude, however, is comparable and indicates a strong electron-withdrawing effect from the side chains [1,9e]. The shifts are only slightly metal dependent.

The ferrocene fragments of Schiff bases **3**–**5** and their chelates seem to possess a distinct higher electron density which does not differ too much from that of unsubstituted ferrocene. Obviously, a change of amine has a more distinct effect than coordination of a transition metal ion. The lack of coplanarity of cyclopentadienyl ring and six-membered metal

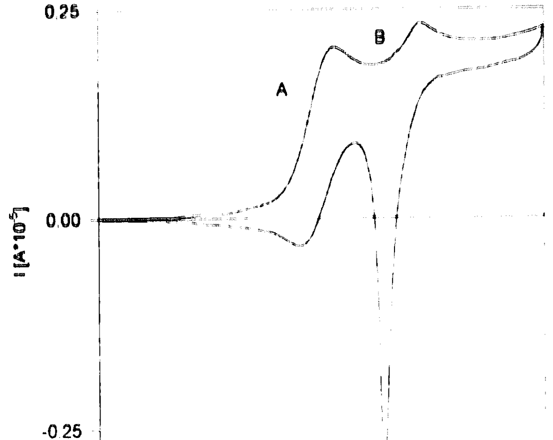


Fig. 3. CV of **5a**. 1 mM in methylene chloride, 0.1 M TBAPC, scan rate: 10 mV s^{-1}.

Table 5
CV data. Potentials are referred to Ag/AgCl. Compounds: 1 mM in methylene chloride, 0.1 M TBAPC. Sweep rate: 10 mV s^{-1}

Compound	E_{ox} (V)	E_{red} (V)	$E_{ox}-E_{red}$ (mV)	$E_{1/2}$ (V)	$E_{1/2}-E_{1/2}(Fc)$ (mV)
ferrocene	0.58	0.51	70	0.54	0
3-ferrocenyl-3-chloro-propenale	0.82	0.65	170	0.73	190
1,1′-bis(3-chloro-propenale)-ferrocene	1.06	0.96	93	1.01	470
1a	0.75	0.64	110	0.70	160
1b	0.70	0.64	60	0.67	130
1c	0.71	0.66	50	0.68	140
1d	0.77	0.63	140	0.70	160
2a	1.00	0.81	190	0.90	360
2b	0.92	0.81	110	0.87	330
3	0.63				50 [a]
3a	0.63	0.53	106	0.58	40
3b	0.66	0.55	111	0.60	60
3c	0.67	0.54	130	0.60	60
4	0.51				−70 [a]
4a	0.55	0.50	50	0.52	−20
5	0.60				20 [a]
5a	0.63	0.54	90	0.59	50
5c	0.61	0.53	80	0.57	30

[a] $E_{ox}=E_{ox}(Fc)$.

cycle might be one reason for the insensitiveness of the ferrocene moiety towards metal ions. In contrast, *N,N*-disubstituted *N′*-ferrocenoyl thioureas show an emphasized redox shift upon complexation [11]. In the latter case the substituted cyclopentadienyl rings are somewhat less distorted and the coordination geometry is nearly planar [10a], allowing conjugation between the two six-membered chelate rings.

4. Supplementary material

Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, Germany, on quoting the depository number CSD-407297.

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