

Available online at www.sciencedirect.com



Inorganica Chimica Acta 358 (2005) 70-76

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and characterization of the bimetallic series $[S_2WS_2Fe(NCS)(X)]^{2-}$ (X = Cl⁻, NCS⁻, N₃⁻)

Eddy Dumas *, Jérôme Marrot, Josseline Jullien, Francis Sécheresse

Institut Lavoisier, IREM, UMR 8637, Université de Versailles, Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles, France

Received 24 May 2004; accepted 10 July 2004 Available online 6 August 2004

Abstract

A series of thioheterobimetallic anions have been synthesized: $[S_2WS_2Fe(NCS)X]^{2-}$ (X = Cl⁻ (1); X = NCS⁻ (2); X = N₃⁻ (3)). The molecular dianions were isolated by substitution in $[S_2WS_2FeCl_2]^{2-}$ of the labile terminal chloro ligands by NCS⁻ and/or N₃⁻. Anions (1) and (3) are the first iron tris-heteroleptic complexes of the well-known $[S_2WS_2FeX_2]^{2-}$ (M = Mo, W) family. The structures of the three molecular anions, isolated as tetraphenylphosphonium salts, are reported, as well as characterization by IR, electronic and electrospray mass spectroscopies.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Thiometalate; Tungsten complexes; Thiocyanate; Azide; Electrospray mass spectrometry

1. Introduction

heterobimetallic The chemistry of Fe-M-S (M = Mo, W) complexes has been extensively developed since the late 1970s, mainly due to their relevance to biological systems involving nitrogenase [1]. At that time, absence of structural characterization of the MoFe protein of nitrogenase led to the synthesis of numerous Fe-M-S clusters presented as potential models consistent with the data available (mainly EXAFS analyses) [2]. Among them, a family of bimetallic molecular anions with the general formula $[S_2MS_2FeX_n]^{2-}$ (M = W and/or Mo; n = 1: X = S₅ [3,4]; n = 2; X = Cl [5-7], SPh [4,7,8], OPh [9], NO[10]) was structurally characterized. Müller et al. [5] pointed out that the $[S_2MS_2FeCl_2]^{2-}$ (M = Mo, W) molecular anion was a possible interesting building unit to generate large multinuclear Fe-M complexes

due to (i) the possible addition reactions at the terminal sulfur atoms, (ii) the presence of coordinatively non-saturated metal atoms and (iii) the substitution reactions which could be carried out at the chloro ligands. The lability of the terminal chloro ligands in $[S_2WS_2FeCl_2]^{2-}$ was used to synthesize the three compounds described herein: (PPh₄)₂[S₂WS₂Fe(Cl)(NC-S)] \cdot (CH₃C(O)CH₃)₂ (1), (PPh₄)₂[S₂WS₂Fe(NCS)₂] (2) and $(PPh_4)_2[S_2WS_2Fe(NCS)(N_3)]$ (3). Compounds 1 and 3 are the first iron tris-heteroleptic complexes of the family. This work was initiated in order to isolate new polythiometallic systems, which could be associated with gold nanoparticles. Our group recently reported the synthesis of a new nanocomposite system formed by the interaction of gold nanoparticles with tetra(oxo)thiotungstates WS_4^{2-} or $WO_2S_2^{2-}$ [11]. Due to the presence of thiocyanato and/or azido ligands, the title dianions should act as effective vibrational spectroscopy probe to follow the reactivity of more sophisticated thiometalate fragments with gold nanoparticles.

^{*} Corresponding author. Tel.: +33139254383; fax: +33139254381. *E-mail address:* dumas@chimie.uvsq.fr (E. Dumas).

2. Experimental

2.1. General procedures

All syntheses were performed under an atmosphere of nitrogen using standard Schlenk-line techniques. Acetonitrile, acetone and methanol were previously distilled from CaH_2 before use. Pentane was degassed prior to use. (PPh₄)₂[WS₄] was synthesized according to previously published procedures [12]. All solid products are air stable.

Elemental analyses of solids were performed by the Service Central d'Analyse du CNRS, Vernaison (France). IR spectra were recorded on a FTIR Nicolet Magna-550 spectrophotometer. UV–Vis spectra were recorded on a Perkin–Elmer lambda 19 spectrophotometer. Thermogravimetric analyses were carried out under nitrogen flow (60 mL/min) with a Perkin–Elmer electrobalance TGA-7 at a heating rate of 5 °C/min.

Electrospray mass spectroscopy (ESMS) spectra were obtained using a HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from analytica of Brandford. The instrument was operated in the negative ion mode. Source parameters were $V_{\text{needle}} = 0$ V, $V_{\text{cyl}} = 3500$ V, $V_{\text{end}} = 3000$ V and $V_{\text{cap}} = 3500$ V. The nebulizing gas (purified air) was heated to approximately 150 °C. The capillary exit voltage was either -80 or -150 V. The mass axis was calibrated using the cluster ions observed from a 50 ng/µL solution of sodium dodecyl sulfate in acetonitrile. Mass spectra were obtained from m/z100 to 1200 by electrospraying 10^{-4} M sample solutions in acetonitrile at a flow rate of 5 µL min⁻¹.

2.2. $(PPh_4)_2[S_2WS_2Fe(NCS)(Cl)] \cdot (CH_3C(O)CH_3)_2$ (1)

A solution of FeCl₂ · 4H₂O (199 mg, 1 mmol) in MeCN (25 mL) was added to a solution of (PPh₄)₂[WS₄] (990 mg, 1 mmol) in MeCN (100 mL). At this stage in the synthesis, (PPh₄)₂[S₂WS₂FeCl₂] can be isolated from the resulting red solution with appropriate treatment or used directly to react with KSCN. KSCN (97 mg, 1 mmol) was added to the red solution. After 1 h, a white precipitate of KCl was removed by filtration. The filtrate was concentrated to ca. 20 mL and diluted with 50 mL of Et_2O to precipitate the crude product. The solid was washed with Et₂O and dried in vacuo. Red crystals of (1) were obtained from a mixture of acetone and pentane maintained at 4 °C overnight. Yield: 930 mg (74%). Anal. Calc. for C₅₅H₅₂NO₂P₂S₅ClFeW (1256.37): W, 14.63; Fe, 4.44; Cl, 2.82; S, 12.76; P, 4.93; N, 1.11; C, 52.58. Found: W, 14.99; Fe, 4.46; Cl, 2.22; S, 11.54; P, 4.53; N, 1.53; C, 52.10%. IR (KBr pellet, cm⁻¹): PPh₄⁺ cations: 1585(m), 1482(m), 1435(s), 1337(m), 1312(m), 1186(m), 1162(m), 1107(vs),

1026(w), 996(m), 751(m), 722(s), 687(s), 527(vs); acetone: 1359(m), 1221(m), v(CO) 1079(s); v(CN)2050(vs); v(CS) 852(vw); $v(WS)_{term}$ 494(w), 485(m); $v(MS)_{br}$ 438(w), 435(sh) 326(w).

2.3. $(PPh_4)_2[S_2WS_2Fe(NCS)_2]$ (2)

Compound **2** was synthesized using the procedure described above with an excess of KSCN (389 mg, 4 mmol). Yield: 880 mg (76%). *Anal.* Calc. for $C_{50}H_{40}N_2P_2S_6FeW$ (1162.84): W, 15.81; Fe, 4.80; S, 16.54; P, 5.33; N, 2.41; C, 51.64. Found: W, 15.19; Fe, 4.69; S, 16.47; P, 3.79; N, 2.46; C, 51.86%. IR (KBr pellet, cm⁻¹): PPh₄+ cations: 1583(m), 1482(m), 1435(s), 1336(m), 1313(m), 1187(m), 1162(m), 1107(vs), 1026(w), 996(m), 753(m), 722(s), 687(s), 616(w), 530(vs); v(CN) 2042(vs), 2023(vs); v(CS) 850(vw); v(WS)_{term} 499(sh), 493(m); v(MS)_{br} 434(w), 428(sh) 317(w).

2.4. $(PPh_4)_2[S_2WS_2Fe(NCS)(N_3)]$ (3)

A solution of NaN₃ (11 mg, 0.175 mmol) in MeOH was added to a solution of compound (1) (200 mg, 0.175 mmol) in CH₃CN (20 mL) and the mixture stirred overnight. The resulting red-brown solution was then concentrated to 5 mL and diluted with 50 mL of Et₂O. The brown precipitate was filtered, washed with Et₂O and recrystallized in 1 day from a mixture of acetone and pentane maintained at 4 °C. Yield: 130 mg (65%). Anal. Calc. for C₄₉H₄₀N₄P₂S₅FeW (1146.79): W, 16.03; Fe, 4.87; S, 13.98; P, 5.40; N, 4.89; C, 51.31. Found: W, 15.59; Fe, 4.81; S, 14.22; P, 5.01; N, 5.02; C, 51.42%. IR (KBr pellet, cm^{-1}): PPh₄⁺ cations: 1583(m), 1483(m), 1434(s), 1334(m), 1313(m), 1188(m), 1163(m), 1108(vs), 1026(w), 996(m), 753(m), 722(s), 687(s), 623(w) 527(vs); v(N₃) 2062(vs); v(CN) 2020(vs); $v(CS) = 847(vw); \delta(N_3) = 621(w); v(WS)_{term} = 502(w),$ 490(m); v(MS)_{br} 437(w), 429(w), 319(w); v(FeN) 391(w).

2.5. X-ray crystallography

X-ray diffraction data sets were collected at room temperature from single crystals of 1 ($0.10 \times 0.06 \times$ 0.04 mm), 2 ($0.68 \times 0.24 \times 0.02$ mm) and 3 ($0.16 \times$ 0.08×0.06 mm) with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [13] based on the method of Blessing [14]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package [15]. Hydrogen atoms were placed at fixed positions using the program HFIX. A summary of crystal data and details of the collection is presented in Table 1. Significant bond distances for 1-3 are given in Table 2.

3. Results and discussion

3.1. Synthesis

Reaction of appropriate amounts of isothiocyanato and/or azido ligand with $[S_2WS_2FeCl_2]^{2-}$ (presynthesized [6] or generated in situ) in acetonitrile results in an exchange of isothiocyanato and/or azido ligand for terminal chloro ligand(s) to produce the new series of thioheterobimetallic compounds (PPh₄)₂[S₂WS₂Fe(NC-S)(Cl]] · (CH₃C(O)CH₃)₂ (1), (PPh₄)₂[S₂WS₂Fe(NCS)₂] (2) and (PPh₄)₂[S₂WS₂Fe(NCS)(N₃)] (3) (Scheme 1). Synthesis of the three compounds clearly illustrates the ability to substitute successively the terminal chloro ligands of the $[S_2WS_2FeCl_2]^{2-}$ fragment to generate asymmetrically coordinated iron centers. A fourth member of the series, containing the $[S_2WS_2Fe(N_3)_2]^{2-}$ molecular anion, was identified in solution by electrospray mass spectroscopy. This compound can be isolated by direct substitution of the terminal chloro ligands in $[S_2WS_2FeCl_2]^{2-}$ or by addition of an excess of sodium azide to **3** (Scheme 1). To date, all crystallization attempts of this new compound remained unsuccessful.

3.2. IR spectra

As already pointed out several years ago, IR vibrational spectra remain a very useful method to character-

Table 1

Table 2

 $Crystal data and structure refinement for (PPh_4)_2[S_2WS_2Fe(NCS)(Cl)] \cdot (CH_3C(O)CH_3)_2 \quad (1), \quad (PPh_4)_2[S_2WS_2Fe(NCS)_2] \quad (2) and (PPh_4)_2[S_2WS_2Fe(NCS)(N_3)] \quad (3)$

	1	2	3
Empirical formula	C ₅₅ ClFeH ₅₂ NO ₂ P ₂ S ₅ W	$C_{50}FeH_{40}N_2P_2S_6W$	C49FeH40N4P2S5W
Molecular weight	1256.37	1162.84	1146.79
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P2_{1}/c$	$P2_{1}/c$
Unit cell dimensions			
<i>a</i> (Å)	11.6797(4)	10.5597(1)	10.6304(1)
b (Å)	12.1878(3)	42.6165(3)	41.9013(1)
c (Å)	12.3975(4)	11.4785(1)	11.1371(2)
α (°)	113.834(1)	90	90
β (°)	106.683(2)	104.727(1)	104.110(1)
γ (°)	103.415(1)	90	90
$V(\text{\AA}^3)$	1419.14(8)	4995.83(7)	4811.10(10)
Ζ	1	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.470	1.546	1.583
$\mu (\mathrm{mm}^{-1})$	2.607	2.942	3.013
Reflections collected/unique (R_{int})	6634/5167 (0.0359)	34725/13033 (0.0563)	33638/12676 (0.0535)
Data/restraints/parameters	5167/3/599	13033/0/556	12676/0/556
Final <i>R</i> indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0664, wR_2 = 0.1476$	$R_1 = 0.0542, wR_2 = 0.0898$	$R_1 = 0.0653, wR_2 = 0.0980$
R indices (all data) ^a	$R_1 = 0.0857, wR_2 = 0.1614$	$R_1 = 0.0979, wR_2 = 0.1033$	$R_1 = 0.1199, wR_2 = 0.1133$
Goodness-of-fit on F^2	1.074	1.069	1.118
Largest difference peak and hole (e $Å^{-3}$)	0.881 and -0.547	0.766 and -1.098	1.030 and -0.639

^a $R_1 = \sum (|F_o| - |F_c|) / \sum |F_c|; \sqrt{\sum w(F_o^2 - F_c^2)^2} / \sum w(F_o^2)^2$ with $1/w = \sigma^2 F_o^2 + (aP)^2 + bP$ and a = 0.0916, b = 0 for 1; a = 0.0265, b = 2.3818 for 2; a = 0.0260, b = 5.1501 for 3.

° 2 2 2		
Selected bond distances (A) in $[S_2WS_2Fe(NCS)(Cl)]^{2-1}$ (1), $[S_2WS_2Fe(NCS)_2]^{2-1}$ (2) and $[S_2WS_2Fe(NCS)(N_3)]^{2-1}$ (3)	Selected bond distances (Å) in $[S_2WS_2Fe(NCS)(Cl)]^{2-1}$ (1), $[S_2WS_2Fe(NCS)_2]^{2-1}$ (2) and $[S_2WS_2Fe(NCS)(N_3)^{2-1}]^{2-1}$	$]^{2-}(3)$

	1	2	3
W–Fe	2.8012(15)	2.7537(8)	2.7459(9)
W-S _{ter}	2.151(4)-2.155(4)	2.1461(16)-2.1476(15)	2.1033(19)-2.1462(18)
W-S _{br}	2.245(3)-2.255(4)	2.2496(13)-2.2511(13)	2.2416(15)-2.2473(16)
Fe-S _{br}	2.295(3)-2.310(4)	2.2950(17)-2.2963(16)	2.2863(19)-2.291(2)
Fe-Cl	2.258(5)		
Fe-N(CS)	1.967(12)	1.949(5)-1.961(5)	1.950(6)
Fe-N(NN)			1.946(7)
N–C	1.026(18)	1.153(7)-1.155(7)	1.146(8)
C–S	1.655(17)	1.599(7)-1.592(7)	1.589(8)
(Fe)N–N(N)			1.196(8)
(FeN)N–N			1.241(9)



Scheme 1. Summary of the dianions isolated in this work by replacement of the terminal chloro ligands in the $[S_2WS_2FeCl_2]^{2-}$ fragment.

ize thiometalate complexes [1]. The two band split of the stretching vibration $v(WS)_{ter}$ (510–480 cm⁻¹ region), observed in the IR spectra of the three title compounds, is characteristic of the bidentate coordination of WS₄²⁻ to the iron center. Presence of strong bands in the 2100–2000 cm⁻¹ is characteristic of thiocyanato and/or azido ligands. The IR spectrum of **1** shows a single strong band at 2050 cm⁻¹ attributed to the v(CN) stretching vibration of the thiocyanato ligand. Two bands, at 2042 and 2023 cm⁻¹, are observed in the IR spectrum of **2**, assigned to the same vibration mode. By analogy, the strong bands observed at 2062 and 2020 cm⁻¹ in the spectrum of **3** are attributed to $v_{as}(N_3^-)$ and v(CN), respectively.

3.3. Electronic spectra

Exchange of NCS⁻ and/or N₃⁻ for the terminal chloro ligands in $[S_2WS_2FeCl_2]^{2-}$ can be easily checked by UV–Vis spectroscopy. Electronic spectra in acetonitrile of $(PPh_4)_2[S_2WS_2FeCl_2]$, (1)–(3) are listed in Table 3. The peak observed at 518 nm for $[S_2WS_2FeCl_2]^{2-}$ is red shifted by substitution of Cl⁻ by NCS⁻ and/or N₃⁻. Comparison of the spectra of $[S_2WS_2Fe(Cl)_{2-n}$ (NCS)_n]²⁻ shows that the shift to lower energy increases (together with a hyperchromic effect) in the order n = 0, 1, 2. Such low energy bands, not observed in the electronic spectrum of WS₄²⁻, were previously attributed to the Fe–L chromophores in analogous iron–tungsten compounds [16]. Two intense peaks, at 277 and 392 nm, are found in the electronic spectrum of WS₄²⁻. Both peaks are attributed to S \rightarrow W transition, the second

peak being unambiguously attributed to the $\pi(t_1) \rightarrow d(2e)$ LMCT transition [1]. Electronic spectra of (PPh₄)₂[S₂WS₂FeCl₂], (1)–(3) show a set of three to five peaks in the 280–420 nm region. This group of bands is therefore assigned to the splitting of the LMCT absorption bands in the WS₄²⁻ fragment perturbed by coordination of a FeX₂ (X = Cl⁻, NCS⁻, N₃⁻) unit [1,16]. In this region, substitution of the terminal chloro ligands induces the appearance of one (compounds **2** and **3**) or two (compound **1**) bands compared to the spectrum of (PPh₄)₂[S₂WS₂FeCl₂].

3.4. Electrospray mass spectroscopy

ESMS spectra of $(PPh_4)_2[S_2WS_2FeCl_2], (1)-(3)$ and the tetraphenylphosphonium salt of the $[S_2WS_2 Fe(N_3)_2]^{2-1}$ molecular dianion have been obtained from 10^{-4} mol L⁻¹ solutions in acetonitrile, with capillary exit voltage values of -80 and -150 V. Typical example of these spectra is presented in Fig. 1 for compound 2. Assignments of the major ESMS signals are given in Table 4. Assignments were confirmed by the experimental values of m/z as well as the isotopic distribution. With a cap exit voltage value of -80 V, ESMS spectra show three sets of peaks (m/z regions: 210-250, 400-430 and 770-830, with a low intensity peak for the later) attributed, respectively, to (i) the molecular dianions of general formula $[S_2WS_2Fe(X_1)(X_2)]^{2-}(X_1, X_2 = Cl^-, NCS^-, N_3^-), (ii)$ the molecular anions of general formula $[S_2WS_2Fe(X_1)]^$ and (iii) the ion-pairs of general formula (PPh₄)[S₂WS₂- $Fe(X_1)(X_2)$ ⁻. ESMS allowed us to characterize the

Table 3

Complexes	λ (nm) (ϵ /L mo	λ (nm) (ϵ/L mol ⁻¹ cm ⁻¹) ^a				
(PPh ₄) ₂ [S ₂ WS ₂ FeCl ₂]	518(500)	415(6240)	372(6390)			286(16100)
(1)	545(797)	414(4745)	368(7345)	335(7760)	316(8073)	285(14260)
(2)	554(1449)	418(6070)	364(13970)	331(13480)		285(14370)
(3)	533(790)	417(6880)	361(10440)	327(12030) ^b		287(13250)

^a A shoulder at about 450 nm is also observed in the four spectra.

^b Very broad band.



Fig. 1. ESMS spectra of $(PPh_4)_2[S_2WS_2Fe(NCS)_2]$ (2) with capillary exit voltage of -80 V.

new $[S_2WS_2Fe(N_3)_2]^{2-}$ molecular dianion for which all crystallization attempts have yet failed. Fragmentation of the parent dianions $[S_2WS_2Fe(X_1)(X_2)]^{2-}$ $(X_1, X_2 = Cl^-, NCS^-, N_3^-)$ generates the $[S_2WS_2Fe(X_1)]^-$ ions in which one chloro or pseudo-halide ligand has been removed. Increasing the cap exit voltage value strengthens the fragmentation process. Peaks attributed to the dianions $[S_2WS_2Fe(X_1)(X_2)]^{2-}$ $(X_1, X_2 = Cl^-, NCS^-, N_3^-)$ are no longer present in the ESMS spectra measured with a capillary exit voltage of -150 V.

3.5. Structures

The structures of the three compounds consist of a molecular dianion $[S_2WS_2Fe(NCS)X]^{2-}$ (X = Cl⁻ (1); X = NCS⁻ (2); X = N₃⁻ (3)) and PPh₄⁺ cations. Compounds **2** and **3** are isostructural and crystallize in the $P2_1/c$ monoclinic space group with close cell parameters, while compound **1** crystallizes in the $P\overline{1}$ triclinic space group with two additional molecules of acetone. The

presence of acetone was confirmed by IR spectroscopy (strong v(CO) band observed at 1079 cm⁻¹). The number of acetone molecules identified by single crystal X-ray diffraction was confirmed by TGA analysis which showed one weight-loss step of 8.91% (theoretical: 9.25%) between room temperature and 100 °C, attributed to the release of the crystallization acetone.

The structures of the dianions $[S_2WS_2Fe(NCS)(Cl)]^{2-1}$ (1), $[S_2WS_2Fe(NCS)_2]^{2-}$ (2) and $[S_2WS_2Fe(NCS)(N_3)]^{2-}$ (3) (Fig. 2) can be described as two tetrahedra, WS_4 and $S_2Fe(NCS)X$ (X = Cl, NCS or N₃), sharing an edge; therefore, WS₄²⁻ plays its common bidentate ligand role for the iron center. The basic $\{S_2WS_2Fe\}$ cores identified in the three molecular anions show comparable structural parameters, among them, and with bimetallic $[S_2WS_2FeX_n]^{2-}$ complexes $(n = 1, X = S_5 [3,4]; n = 2,$ X = Cl [5b,6], SPh [4], NO [10]) previously characterized. The only noticeable structural difference between the three title compounds deals with the $W \cdots Fe$ distances, nearly 0.05 A longer in 1 compared with 2 and 3. Atoms of the $\{W-(\mu-S)_2-Fe\}$ fragment are nearly coplanar with a maximum deviation of 0.03, 0.08 and 0.08 Å from the least-squares plane for 1-3, respectively. The S-W-S angles in WS_4^{2-} are close to the ideal T_d symmetry (range: 105.75(13)–110.83(13)° for 1, 106.41(5)–111.27(6)° for 2 and $106.46(6) - 110.79(7)^{\circ}$ for **3**). The W···S distances can be divided in two pairs of terminal and bridging bonds, the former nearly 0.1 A shorter than the later (Table 2). The {S₂FeX₂} unit (X = Cl or N) is comparatively more distorted from the ideal T_d symmetry with the X-Fe-Y angles (X, Y = Cl, N or S) ranging between 102.39(14)° and 112.54(17)° for 1, 103.44(5)° and 115.40(17)° for 2, 103.55(7)° and 114.0(2)° for 3. The Fe–Cl distance (2.258(5) Å) found in 1 is consistent with the average terminal metal-ligand distances measured in $[S_2WS_2FeCl_2]^{2-}$ anions (in which a crystal disorder of Fe

Table 4

Assignments of the major ESMS signals of $(PPh_4)_2[S_2WS_2FeCl_2]$, $(PPh_4)_2[S_2WS_2Fe(NCS)(Cl)] \cdot (CH_3C(O)CH_3)_2$ (1), $(PPh_4)_2[S_2WS_2Fe(NCS)_2]$ (2), $(PPh_4)_2[S_2WS_2Fe(NCS)_2]$ (3) and $(PPh_4)_2[S_2WS_2Fe(N_3)_2]^a$ in CH₃CN (capillary exit voltage: -80 V)

Compounds	m/z (Exp.) ^b	m/z (Theo.) ^c	Assignment
(PPh ₄) ₂ [S ₂ WS ₂ FeCl ₂]	219.1	218.9	$[S_2WS_2FeCl_2]^{2-}$
	402.5	402.7	[S ₂ WS ₂ FeCl] ⁻
1	230.4	230.4	$[S_2WS_2Fe(NCS)(Cl)]^{2-}$ (1)
	402.3	402.7	$[S_2WS_2FeCl]^-$
	425.4	425.7	$[S_2WS_2Fe(NCS)]^-$
2	241.9	241.9	$[S_2WS_2Fe(NCS)_2]^{2-}$ (2)
	425.8	425.7	$[S_2WS_2Fe(NCS)]^-$
3	233.9	233.9	$[S_2WS_2Fe(NCS)(N_3)]^{2-}$ (3)
	409.7	409.8	$[S_2WS_2Fe(N_3)]^-$
	425.7	425.7	$[S_2WS_2Fe(NCS)]^-$
$(PPh_4)_2[S_2WS_2Fe(N_3)_2]^a$	225.7	225.9	$[S_2WS_2Fe(N_3)_2]^{2-}$
	409.7	409.8	$[S_2WS_2Fe(N_3)]^-$

^a Formula suggested by ESMS.

^b Highest intensity peak.

^c Most abundant isotopic mass.



Fig. 2. Molecular dianions (a) $[S_2WS_2Fe(NCS)(CI)]^{2-}$ (1), (b) $[S_2WS_2Fe(NCS)_2]^{2-}$ (2) and (c) $[S_2WS_2Fe(NCS)(N_3)]^{2-}$ (3) (thermal ellipsoids at 30% probability).

and W as well as terminal sulfurs and chlorides occurs) [5b,6].

Fe–N(CS) and Fe–N(NN) distances are similar in the three molecular dianions. The thiocyanato ligands in **2** and **3** display comparable classical N–C and C–S distances. In **1**, the N–C distance is comparatively nearly 0.13 Å shorter and the C–S slightly longer. The thiocyanato and azido ligands are nearly linear in the three title dianions (N–C–S and N–N–N angles between 174.8(7)° and 179.8(6)°). The Fe–NCS group is slightly bent in **1** and **3** (168.9(13)° and 165.7(6)°, respectively). While one of the Fe–NCS groups is comparably bent

at 169.0(5)° in **2**, the bending is more important in the remaining Fe–NCS group (158.1(5)°), a trend even more pronounced for the Fe–N₃ group in **3** (Fe–N–N angle: 134.7°).

4. Conclusion

The three compounds presented here further enhance the reactivity perspectives of the $[S_2WS_2FeCl_2]^{2-}$ dianion. Stepwise substitution of the terminal chloro ligands by pseudo-halide ions like NCS⁻ or N₃⁻ allowed us to synthesize the first iron tris-heteroleptic complexes of the $[S_2WS_2FeX_2]^{2-}$ family. Both the synthesis of new derivatives of the $[S_2WS_2FeCl_2]^{2-}$ fragment (replacement of the chloro, or more generally halide, terminal ligand by various potentially bridging ligands) and the study of the reactivity of the dianions presented here, for example with various transition metals are currently investigated in our group. The thiocyanato ligands are well-known for their bonding versatility and have already proven to be effective ligands to generate polymeric thiometallic structures [17]. Azido ligands also show versatile bridging coordination modes and magnetic coupler properties [18]. Hence, the title dianions offer new perspectives for the synthesis of multimetallic molecular or extended systems with potential interesting magnetic properties and should allow the study of the influence of thiometalate fragments on these properties.

5. Supplementary material

CCDC-239354 (1), CCDC-239355 (2) and CCDC-239356 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.ca;.ac.uk].

Acknowledgments

We gratefully thank Vincent Steinmetz for ESMS measurements.

References

- A. Müller, E. Diemann, R. Jostes, H. Bögge, Angew. Chem., Int. Ed. 20 (1981) 934.
- [2] (a) S.P. Cramer, K.O. Hodgson, W.O. Gillum, L.E. Mortenson, J. Am. Chem. Soc. 100 (1978) 3398;
 (b) S.P. Cramer, W.O. Gillum, K.O. Hodgson, L.E. Mortenson, E.I. Stiefel, J.R. Chisnell, W.J. Brill, V.K. Shah, J. Am. Chem. Soc. 100 (1978) 3814.

- [3] D. Coucouvanis, N.C. Baenziger, E.D. Simhon, P. Stremple, D. Swenson, A. Kostikas, A. Simopoulos, V. Petrouleas, V. Papaef-thymiou, J. Am. Chem. Soc. 102 (1980) 1730.
- [4] D. Coucouvanis, P. Stremple, E.D. Simhon, D. Swenson, N.C. Baenziger, M. Draganjac, L.T. Chan, A. Simopoulos, V. Papaefthymiou, A. Kostikas, V. Petrouleas, Inorg. Chem. 22 (1983) 293.
- [5] (a) A. Müller, H. Bögge, H.-G. Tölle, R. Jostes, U. Schimanski, M. Dartmann, Angew. Chem., Int. Ed. 19 (1980) 654;
 (b) A. Müller, H.-G. Tölle, H. Bögge, Z. Anorg. Allg. Chem. 471 (1980) 115.
- [6] A. Müller, H. Bögge, U. Schimanski, M. Penk, K. Nieradzik, M. Dartmann, E. Krickemeyer, J. Schimanski, C. Römer, M. Römer, H. Dornfeld, U. Wienböker, W. Hellman, M. Zimmermann, Monatsch. Chem. 120 (1989) 367.
- [7] (a) R.H. Tieckelmann, H.C. Silvis, T.A. Kent, B.H. Huynh, J.V. Waszczak, B.-K. Teo, B.A. Averill, J. Am. Chem. Soc. 102 (1980) 5550;

(b) A. Müller, R. Jostes, H.G. Tölle, A. Trautwein, E. Bill, Inorg. Chim. Acta 46 (1980) L121.

- [8] D. Coucouvanis, E.D. Simhon, D. Swenson, N.C. Baenziger, J. Chem. Soc., Chem. Commun. (1979) 361.
- [9] B.-K. Teo, M.R. Antonio, R.H. Tieckelmann, H. Craig Silvis, B.A. Averill, J. Am. Chem. Soc. 104 (1982) 6126.

- [10] A. Müller, P. Stolz, H. Bögge, S. Sarkar, K. Schmitz, A. Fangmeier, H. Büker, W. Twistel, Z. Anorg. Allg. Chem. 559 (1988) 57.
- [11] C.R. Mayer, S. Neveu, C. Simonnet-Jégat, C. Debiemme-Chouvy, V. Cabuil, F. Sécheresse, J. Mater. Chem. 13 (2003) 338.
- [12] K.E. Howard, J.R. Lockemeyer, M.A. Massa, T.B. Rauchfuss, S.R. Wilson, X. Yang, Inorg. Chem. 29 (1990) 4385.
- [13] G.M. Sheldrick, SADABS; Program for Scaling and Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1997.
- [14] R. Blessing, Acta Cryst. A51 (1995) 33.
- [15] G.M. Sheldrick, SHELX-TL version 5.03, Software Package for the Crystal Structure Determination, Siemens Analytical X-ray Instrument Division, Madison, WI, USA, 1994.
- [16] D. Coucouvanis, Acc. Chem. Res. 14 (1981) 201.
- [17] (a) J.-M. Manoli, C. Potvin, F. Sécheresse, S. Marzak, J. Chem. Soc., Chem. Commun. (1986) 1557;
 (b) C. Potvin, J.-M. Manoli, F. Sécheresse, S. Marzak, Inorg. Chem. 26 (1987) 4370;
 (c) J.-M. Manoli, C. Potvin, F. Sécheresse, S. Marzak, Inorg. Chim. Acta (1988) 257.
- [18] (a) See, for example, recent polymeric iron/azide complexes: A. Fu, X. Huang, J. Li, T. Yuen, C.L. Lin, Chem. Eur. J. 8 (2002) 2239;
 (b) S. Konar, E. Zangrando, M.G.B. Drew, T. Mallah, J. Ribas, N.R. Chaudhuri, Inorg. Chem. 42 (2003) 5966.