Generating Structural Motifs between Three-Dimensional Solids and Discrete Species Based on the {CuNCS} Unit: $(PPh_4)[(ReS_4)Cu_2(NCS)_2]$, $(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]$, and $(PPh_4)_2[(ReS_4)_2Cu_2(NCS)_2]$

Achim Müller,* Achim Hildebrand, Erich Krickemeyer, Mohammed Isaque Khan, Michael Penk, Hartmut Bögge, and Francis Sécheresse

Dedicated to Professor Dr. Peter Jutzi on the occasion of his 60th birthday.

Abstract: The reaction of $(PPh_4)ReS_4$ or $(NEt_4)ReS_4$ with CuNCS (in different solvents and with different relative amounts of reactants) yielded black crystals of $(PPh_4)[(ReS_4)Cu_2(NCS)_2]$ (**1**), $(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]$ (**2**) and $(PPh_4)_2[(ReS_4)_2Cu_2(NCS)_2]$ (**3**). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ [$a = 21.488(6)$ Å, $b = 11.142(4)$ Å, $c = 12.860(5)$ Å, $\beta = 90.66(3)^\circ$, $V = 3079(2)$ Å^3, $Z = 4$, $R = 0.058$ and $R_w = 0.063$ for 5802 reflections with $F > 4\sigma(F)$], compound **2** in the monoclinic space group $P2_1/n$ [$a = 10.551(4)$ Å, $b = 14.849(6)$ Å, $c = 22.782(11)$ Å, $\beta = 92.35(4)^\circ$, $V = 3566(3)$ Å^3, $Z = 4$, $R = 0.078$ and $R_w = 0.056$ for 3006 reflections with $F > 4.5\sigma(F)$] and compound **3** in the triclinic space group $P\bar{1}$ [$a = 10.901(3)$ Å, $b = 10.981(3)$ Å, $c = 12.296(3)$ Å, $\alpha = 109.20(2)$, $\beta = 96.40(2)$, $\gamma = 98.17(2)^\circ$, $V = 1356.0(6)$ Å^3, $Z = 1$, $R = 0.056$ and $R_w = 0.061$ for 5016 reflections with $F > 4\sigma(F)$]. The structure of the anion in **1** consists of pairs of infinite CuNCS zigzag chains connected by ReS_4^- groups, thus generating twelve-membered rings running almost parallel to the *b* axis. In **2**, one $Cu(NCS)_2$ and two Cu(NCS) units are linked by ReS_4^- groups leading to twelve-membered and novel, unusual sixteen-membered rings alternately arranged in a linear strand. In the discrete complex of **3**, two terminal ReS_4^- groups stabilize one eight-membered $(CuNCS)_2$ ring. An interesting aspect of the present chemistry is the possibility of excision or linking of fragments from a solid-state structure (CuNCS) in which robust entities are interlinked in different ways.

Keywords: copper · N ligands · inorganic polymers · rhenium · S ligands

Introduction

Thiometalates of the type MS_4^{n-} (M = Re with $n = 1$; M = Mo, W with $n = 2$; M = V, Nb, Ta with $n = 3$) have been extensively used for the synthesis of heterometallic compounds, for example, by direct reaction with transition metal cations.[1–3] The first corresponding discrete complex reported was $[Ni(WS_4)_2]^{2-}$.[1b] In most related cases the transition metal centres (Fe, Ni, Co, Pd, Pt etc.) are bonded to the thiometalate by two of its sulfur atoms. The reaction with Cu^{II} ions is unique with regard to the reducing property of MS_4^{2-} ions (M = Mo, W) versus Cu^{II}, which leads to the catena compounds $(NH_4)Cu(MS_4)$[4] in which the CuS_4 and MS_4 tetrahedra are linked through S–S edges to form infinite chains. Only a few structurally characterized one-dimensional solids based on the MS_4^{2-} moiety (and other ligands) are known so far. In these structures extra ligands bonded to copper centres are represented exclusively by halide or pseudohalide ions (X^-) that are soft enough to coordinate to neighbouring Cu centres, resulting in the formation of CuXCu units. Here we report three copper–rhenium–sulfur compounds based on the ReS_4^- ligand with different Cu/ReS_4 stoichiometries[5] and some unprecedented structural features. The ReS_4^- ligand was expected to demonstrate a significantly different coordination behaviour compared with the MoS_4^{2-} and WS_4^{2-} anions, which have a higher charge density. Our main interest is to show that it is possible to generate structural motifs between three-dimensional solids and discrete units, with the ReS_4^- ion as an excision or linking agent for solid $\{CuNCS\}_\infty$-containing interlinked linear robust CuNCS units.

---

[*] A. Müller, A. Hildebrand, E. Krickemeyer, M. Penk, H. Bögge
Fakultät für Chemie der Universität
Lehrstuhl für Anorganische Chemie I
Postfach 100131, D-33501 Bielefeld (Germany)
Fax: (+49)521-106-6003
E-mail: amueller@cheops.chemie.uni-bielefeld.de

M. I. Khan
Chemistry Division, Illinois Institute of Technology
Chicago, IL 60676 (USA)

F. Sécheresse
Institut de Reactivité, Electrochimie et Microporosités, IREM
UMR CO173, Batiment Lavoisier, 45, Avenue des Etats-Unis
78035 Versailles (France)

Experimental Section

Reactions were routinely carried out under an Argon atmosphere. $(NEt_4)ReS_4$ and $(PPh_4)ReS_4$ were prepared according to methods given in the literature.[2a, 6] All other chemicals were of pro-analysis quality and used as received from commercial sources. Solvents were dried by standard methods.

Preparation of $(PPh_4)[(ReS_4)Cu_2(NCS)_2]$ (1) and $(PPh_4)_2[(ReS_4)_2Cu_2(NCS)_2]$ (3): A mixture of $(PPh_4)ReS_4$[6] (100 mg, 0.15 mmol), CuNCS (300 mg, 2.47 mmol) and acetone (50 mL) was stirred in a closed flask for 1 d at ambient temperature under an Argon atmosphere. After filtration, the red-violet solution was left in an open 100 mL Erlenmeyer-flask (narrow neck). When the volume of the solution had reached about 15 mL, due to the slow evaporation process, black monoclinic crystals of **1** were filtered off, washed with 2-propanol and diethylether, and dried in air. (A few yellow-brown crystals also precipitated and were mechanically separated.) Yield: 42 mg (31 % based on Re); $C_{26}H_{20}Cu_2N_2PReS_6$ (897.1): calcd C 34.81, H 2.25, N 3.12, S 21.45; found C 34.62, H 2.19, N 3.62, S, 20.0; IR data (solid/KBr pellet): $\tilde{\nu} = 2128$ (m), 2111 (s), 2083 (sh, $\tilde{\nu}$(CN)), 515 cm^{-1} (sh, $\tilde{\nu}(ReS_{term})$).

Black prismatic crystals of **3** (see also ref. [12]) were obtained in a similar way, but with a larger (stoichiometric) amount of $(PPh_4)ReS_4$ corresponding to the formula of **3**. Yield: 60 mg (51 % based on Re); $C_{50}H_{40}Cu_2N_2P_2Re_2S_{10}$ (1551.0): calcd C 38.72, H 2.60, N 1.81, S 20.67; found C 38.10, H 2.82, N 1.64, S 19.8; IR data (solid/KBr pellet): $\tilde{\nu} = 2111$ (s), 2092 (m, $\tilde{\nu}$(CN)), 514 (m), 506 cm^{-1} (m, $\tilde{\nu}(ReS_{term})$).

Preparation of $(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]$ (2): A reaction mixture of $(NEt_4)ReS_4$[2a] (44 mg, 0.10 mmol), CuNCS (50 mg, 0.41 mmol) and acetone (35 mL) was stirred in a closed flask for 1 d at ambient temperature under an Argon atmosphere. After filtration, toluene (30 mL) was added to the red-violet solution and the mixture was allowed to stand in a 100 mL Erlenmeyer-flask (wide neck) covered with a watch glass for 7 – 10 d. The precipitated black needlelike crystals of **2** were filtered off, washed with 2-propanol and diethylether, and dried in air. (Some of the yellow-brown crystals mentioned above were mechanically separated.) Yield: 55 mg (55.7 % based on Re); $C_{20}H_{40}Cu_3N_6ReS_8$ (998.0): calcd C 24.07, H 4.04, N 8.42, S 25.71; found C 24.40, H 3.70, N 8.25, S 25.0; IR data (solid/KBr pellet): $\tilde{\nu} = 2115$ (m), 2090 cm^{-1} (s, $\tilde{\nu}$(CN)).

In all three cases the $\tilde{\nu}$(CS) bands are not identified because of their extreme low intensity and the presence of other bands in the corresponding region.

Structure determination:[7] Crystals suitable for X-ray crystal determination were selected directly from the precipitates. Data were collected with a Siemens R3m/V four-circle diffractometer by means of ω scans. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ scan) was applied. The three structures were solved by Direct Methods. The phenyl rings in **1** and **3** were refined as rigid hexagons with hydrogen atoms (C – C = 1.395 Å, C – H = 0.96 Å). All computations were performed with the program package SHELXTL-PLUS (VMS).[8] Cell dimensions, specific parameters pertaining to the data collection and details of refinement are given in Table 1. Selected interatomic distances and angles of the three anions are given in Tables 2 and 3, respectively.

Table 1. Crystallographic data for $(PPh_4)[(ReS_4)Cu_2(NCS)_2]$ (**1**), $(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]$ (**2**) and $(PPh_4)_2[(ReS_4)_2Cu_2(NCS)_2]$(**3**).

	1	**2**	**3**
formula	$C_{26}H_{20}Cu_2N_2PReS_6$	$C_{20}H_{40}Cu_3N_6ReS_8$	$C_{50}H_{40}Cu_2N_2P_2Re_2S_{10}$
M_r	897.1	997.9	1550.9
colour	black	black	black
crystal size [mm]	0.6 × 0.4 × 0.35	0.3 × 0.15 × 0.05	0.5 × 0.25 × 0.15
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [Å]	21.488(6)	10.551(4)	10.901(3)
b [Å]	11.142(4)	14.849(6)	10.981(3)
c [Å]	12.860(5)	22.782(11)	12.296(3)
α [°]			109.20(2)
β [°]	90.66(3)	92.35(4)	96.40(2)
γ [°]			98.17(2)
V [Å^3]	3079(2)	3566(3)	1356(1)
Z	4	4	1
radiation $Mo_{K\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	294	294	294
d_{calcd} [g cm^{-3}]	1.935	1.859	1.899
abs coeff [cm^{-1}]	58.14	56.76	57.5
reflections collected	8117	5613	7095
observed reflections	5802 [$F > 4.0\sigma(F)$]	3006 [$F > 4.5\sigma(F)$]	5016 [$F > 4.0\sigma(F)$]
R[a]/R_w[b]	0.058/0.063	0.078/0.056	0.056/0.061

[a] $R = \Sigma||F_0 - F_c||/\Sigma|F_0|$; [b] $R_w = [(\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $1/w = \sigma^2(F_0) + 0.0001F_o^2$

Table 2. Selected interatomic distances (Å) for $[(ReS_4)Cu_2(NCS)_2]^-$ in **1**, $[(ReS_4)Cu_3(NCS)_4]^{2-}$ in **2** and $[(ReS_4)_2Cu_2(NCS)_2]^{2-}$ in **3**.

Compound **1**	Re – Cu1	2.631(1)	Re – Cu2	2.658(2)
	Re – S1	2.213(2)	Re – S2	2.160(2)
	Re – S3	2.167(2)	Re – S4	2.101(3)
	Cu1 – S1	2.252(3)	Cu1 – S3	2.268(3)
	Cu1 – S5	2.464(3)	Cu1 – N2A	1.915(7)
	Cu2 – S1	2.257(3)	Cu2 – S2	2.267(3)
	Cu2 – S6	2.463(3)	Cu2 – N1A	1.922(7)
	S5 – C25	1.650(9)	S6 – C26	1.635(8)
	N1 – C25	1.140(12)	N2 – C26	1.146(10)
Compound **2**	Re – Cu1	2.616(3)	Re – Cu2	2.637(3)
	Re – Cu3	2.658(3)	Re – S1	2.207(5)
	Re – S2	2.211(5)	Re – S3	2.156(5)
	Re – S4	2.148(6)	Cu1 – S1	2.263(6)
	Cu1 – S4	2.259(6)	Cu1 – N1	1.884(20)
	Cu1 – S7A	2.603(6)	Cu2 – S1	2.285(6)
	Cu2 – S2	2.284(5)	Cu2 – N2	1.922(16)
	Cu2 – S8B	2.571(6)	Cu3 – S2	2.291(5)
	Cu3 – S3	2.271(6)	Cu3 – N3	1.973(18)
	Cu3 – N4	1.984(16)	S5 – C1	1.629(22)
	S6 – C2	1.630(21)	S7 – C3	1.596(23)
	S8 – C4	1.653(19)	N1 – C1	1.139(28)
	N2 – C2	1.136(26)	N3 – C3	1.159(28)
	N4 – C4	1.146(24)		
Compound **3**	Re – Cu	2.629(1)	Re – S1	2.093(4)
	Re – S2	2.094(3)	Re – S3	2.173(3)
	Re – S4	2.157(3)	Cu – S3	2.256(4)
	Cu – S4	2.252(3)	Cu – N	1.958(7)
	Cu – S5A	2.521(4)	S5 – C25	1.648(8)
	S5 – CuA	2.521(4)	C25 – N	1.146(10)

Results and Discussion

The reaction of $(PPh_4)ReS_4$ or $(NEt_4)ReS_4$ with CuNCS in different solvents and with different relative amounts of reactants yielded black crystals of $(PPh_4)[(ReS_4)Cu_2(NCS)_2]$ (**1**), $(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]$ (**2**) and $(PPh_4)_2[(ReS_4)_2Cu_2(NCS)_2]$ (**3**), respectively, in reasonable yields. In all cases the crystal structure could be determined. An interesting aspect of this type of investigation is the question whether the obtained dimensionality of the compounds built up from MS_4 (M = Mo, W, Re) and Cu halide or pseudohalide moieties (see Table 4) can be planned and, in particular, how the reaction of the soft ligand ReS_4^- with chainlike assemblies of copper(I)thiocyanate can be influenced. In this context it is interesting to note that the colourless modification of crystalline CuNCS consists of mutually interlinked linear formations of

Table 3. Selected angles (°) for $[(ReS_4)Cu_2(NCS)_2]^-$ in **1**, $[(ReS_4)Cu_3(NCS)_4]^{2-}$ in **2** and $[(ReS_4)_2Cu_2(NCS)_2]^{2-}$ in **3**.

Compound **1**	Cu1-Re-Cu2	92.1(1)	S1-Re-S2	109.2(1)
	S1-Re-S3	109.8(1)	S2-Re-S3	108.2(1)
	S1-Re-S4	109.2(1)	S2-Re-S4	110.3(1)
	S3-Re-S4	110.2(1)	S1-Cu1-S3	104.9(1)
	S1-Cu1-S5	105.4(1)	S3-Cu1-S5	111.8(1)
	S1-Cu1-N2A	121.9(3)	S3-Cu1-N2A	115.3(2)
	S5-Cu1-N2A	96.8(2)	S1-Cu2-S2	104.0(1)
	S1-Cu2-S6	105.9(1)	S2-Cu2-S6	105.9(1)
	S1-Cu2-N1A	120.6(2)	S2-Cu2-N1A	115.0(2)
	S6-Cu2-N1A	104.2(2)	Re-S1-Cu1	72.2(1)
	Re-S1-Cu2	73.0(1)	Cu1-S1-Cu2	115.3(1)
	Re-S2-Cu2	73.7(1)	Re-S3-Cu1	72.7(1)
	Cu1-S5-C25	103.3(3)	Cu2-S6-C26	102.3(3)
	C25-N1-Cu2B	173.8(7)	C26-N2-Cu1B	173.1(7)
	S5-C25-N1	178.0(8)	S6-C26-N2	178.4(8)
Compound **2**	Cu1-Re-Cu2	86.9(1)	Cu1-Re-Cu3	173.9(1)
	Cu2-Re-Cu3	97.0(1)	S1-Re-S2	109.4(2)
	S1-Re-S3	107.9(2)	S2-Re-S3	110.3(2)
	S1-Re-S4	110.4(2)	S2-Re-S4	109.2(2)
	S3-Re-S4	109.5(2)	S1-Cu1-S4	104.5(2)
	S1-Cu1-N1	122.0(6)	S4-Cu1-N1	122.4(6)
	S1-Cu1-S7A	101.9(2)	S4-Cu1-S7A	107.1(2)
	N1-Cu1-S7A	95.3(6)	S1-Cu2-S2	104.2(2)
	S1-Cu2-N2	116.3(5)	S2-Cu2-N2	126.2(5)
	S1-Cu2-S8B	105.3(2)	S2-Cu2-S8B	102.9(2)
	N2-Cu2-S8B	99.1(5)	S2-Cu3-S3	103.5(2)
	S2-Cu3-N3	119.6(5)	S3-Cu3-N3	108.4(5)
	S2-Cu3-N4	108.1(5)	S3-Cu3-N4	107.8(5)
	N3-Cu3-N4	108.7(7)	Re-S1-Cu1	71.6(2)
	Re-S1-Cu2	71.9(2)	Cu1-S1-Cu2	105.1(2)
	Re-S2-Cu2	71.8(2)	Re-S2-Cu3	72.4(2)
	Cu2-S2-Cu3	120.1(2)	Re-S3-Cu3	73.8(2)
	Re-S4-Cu1	72.8(2)	C3-S7-Cu1A	100.9(8)
	C4-S8-Cu2B	100.0(7)	Cu1-N1-C1	163.1(20)
	Cu2-N2-C2	163.6(17)	Cu3-N3-C3	166.0(16)
	Cu3-N4-C4	170.6(16)	C5-N5-C6	113.2(16)
Compound **3**	S1-Re-S2	107.9(1)	S1-Re-S3	110.0(1)
	S2-Re-S3	110.0(1)	S1-Re-S4	108.5(1)
	S2-Re-S4	110.2(1)	S3-Re-S4	110.1(1)
	S3-Cu-S4	103.9(1)	S3-Cu-N	118.4(3)
	S4-Cu-N	116.6(3)	S3-Cu-S5A	106.9(1)
	S4-Cu-S5A	110.0(1)	N-Cu-S5A	100.5(3)
	Re-S3-Cu	72.8(1)	Re-S4-Cu	73.2(1)
	C25-S5-CuA	97.2(4)	S5-C25-N	177.7(9)
	Cu-N-C25	163.5(8)		

Table 4. Dimensionality of structurally characterized polymeric compounds containing Cu atoms and MS_4 ligands with increasing Cu/(MS_4) ratio.

	Dimensionality	Reference
$(NMe_4)_2[(MoS_4)Cu_2(CN)_2]$	1D	10
$(NEt_4)_2[(WS_4)Cu_3(NCS)_3]$	1D	11
$(NEt_4)_2[(ReS_4)Cu_3I_4]$	1D	12
$[(MS_4)(bpy)_2Cu_{3.75}Cl_{1.75}]$	1D	13
$(PPh_4)_2[(MoS_4)Cu_4Br_4]\cdot Me_2CO$	1D	14
$(PPh_4)_2[(MS_4)Cu_4(NCS)_4]$[a]	2D	11, 15
$(NMe_4)_2[(MS_4)Cu_4(NCS)_4]$[a]	3D	16
$(NPr_4)_2[(MS_4)Cu_4Cl_4]$[a]	1D	17
$(NEt_4)_3[(WS_4)Cu_4(NCS)_5]$	1D	11
$(PPh_4)_2[(ReS_4)Cu_4I_5]$	1D	18
$(NPr_4)_2[(ReS_4)Cu_5I_6]$	1D	12

[a] M = Mo, W.

CuNCS and even a $\{CuNCS\}_\infty$ chain as a structural motif. Therefore its reaction with ReS_4^- can be considered as an excision-type one.[9] The size of the CuNCS assemblages in the resulting product should, for instance, be influenced by their concentration or abundance in solution, whereby the nature of the resulting product will in any case be strongly influenced by the relative overall amounts of reactants and the type of solvent(s). Intact large $\{CuNCS\}_\infty$-type chain assemblies only occur in the final structure if a large excess of CuNCS is used (as in the synthesis of **1**). However, the experimental information available up to now does not suffice for a complete understanding of all details.

Structure of compound 1: The packing of **1** (Figure 1a) shows the stacking of the PPh_4^+ cations and the alignment of the anionic chains parallel to the *b* axis. The anion of **1** contains infinite CuNCS chains running almost parallel to each other along the *b* axis of the unit cell as represented in Figures 1a and 1b. (Note that a high excess of CuCNS, containing the $\{CuNCS\}_\infty$ chains as structural motif, was used for the synthesis.) The chains are fixed, cross-linked by ReS_4^- groups at two doubly bridging copper atoms belonging to the two different chains through the sulfur atoms of the ReS_4^- units. This cross-linking generates well-defined twelve-membered rings connected to one another across the ReS_4^- groups. These large rings are constituted of, alternatly, copper and sulfur atoms, and NCS groups. A segment of the polymeric anion in **1** is shown in Figure 1b. Bond lengths and angles are given in Tables 2 and 3. Two adjacent edges of the ReS_4^- tetrahedron (involving three sulfur atoms) are bridged by two copper atoms giving rise to a short terminal Re=S bond (2.101(3) Å, Figure 1a and 1b). Few examples containing only two Cu atoms in a kind of *cis* position have been reported to date, for example, the compounds $[(MOS_3)Cu_2(PPh_3)_3]$ (M = Mo, W).[19] In these discrete species the *cis* configuration of the copper atoms is attributed to the presence of a terminal (hard) oxygen atom, which shows no tendency to bind to a soft acid such as Cu^I. The presence of the terminal Re=S bond in **1** is a consequence not only of the comparably low electron density on the sulfur atoms of the ReS_4^- group, but also of the special polymeric structure of the compound with a Cu/Re stoichiometry of 2:1. The Re–Cu distances of 2.631(1)–2.658(2) Å are comparable with the values found in other polymeric species (2.638(4)–2.712(4) Å in $\{(ReS_4)Cu_4I_5^{2-}\}_\infty$,[18] 2.674(1)–2.678(2) Å in $\{(ReS_4)Cu_5I_6^{2-}\}_\infty$[12] and 2.614(4)–2.685(4) Å in $\{(ReS_4)Cu_3I_4^{2-}\}_\infty$[12]).

The specific type of interaction of the Cu atoms with the thiocyanate ligand implies that the large rings derive from infinite chains built up from CuNCS units that are cross-linked by S-Re-S bridges. This description correlates with the fact that the two Cu atoms connected to the same ReS_4^- tetrahedron are both N- and S-bonded to thiocyanate ligands and interestingly that the ReS_4^- groups stabilize the ⋯CuNCS⋯CuNCS⋯ chains. Twelve-membered rings have also been observed in the polymeric tungsten species $\{(WS_4)Cu_4(NCS)_5\}_\infty$.[11]

Structure of compound 2: A segment of the structure of the polymeric anion in **2** with a Cu/Re ratio of 3:1 is represented

0947-6539/98/0410-1934 $ 17.50+.50/0

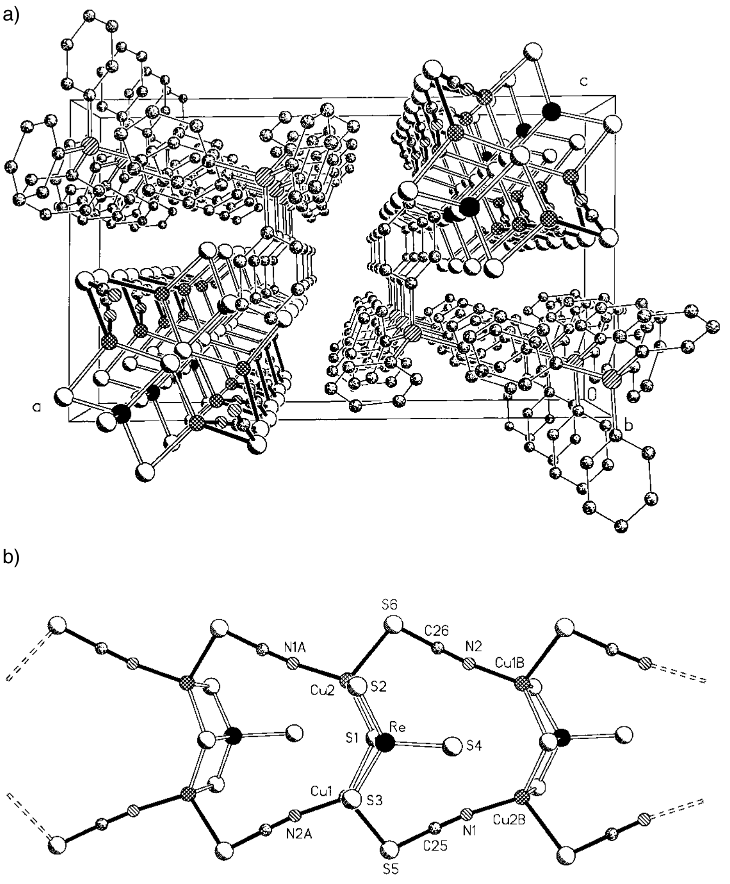

Figure 1. a) View of the packing of **1** showing the alignment of the PPh$_4^+$, ReS$_4^-$ and CuNCS moieties. b) Segment of the polymeric anions of **1** showing the two CuNCS type chains linked by ReS$_4^-$ units.

in Figure 2. As in the case of **1,** the anions in **2** contain two individual strand motifs that run parallel to the crystallographic *a* axis and are essentially built up by Cu(NCS) and Cu(NCS)$_2$ units intersected by S atoms as shown in Figure 2. This is due to the fact that a much smaller amount of CuNCS was used for the synthesis compared with that of **1**, which has intact CuNCS chains. Interstrand cross-linking is provided by the ReS$_4^-$ groups that interconnect the Cu atoms between two individual strands, whereby all four sulfur atoms are involved. In contrast to **1** the ReS$_4^-$ groups do not only act as interstrand cross-links. One of the four sulfur atoms (S1) bridges two Cu atoms within one strand (Cu1 and Cu2) thus forming part of an infinite ···NCS-Cu-···S-Cu-···SCN··· chain. Two sulfur atoms of the ReS$_4$ group (S1 and S2) act as μ_3 bridges and while the remaining two (S3 and S4) are μ_2-bridging. The orientation of the bridging NCS groups also differs in that they are approximately parallel in **1** and antiparallel in **2**. While the anions of **1** and **2** both contain twelve-membered rings, the latter displays, alternating with these, additional sixteen-membered rings as shown in Figure 2. This type of sixteen-membered ring is unprecedented. With respect to relevant thiometalate compounds with *catena* structures, only twelve-membered rings have been reported so far.[10]

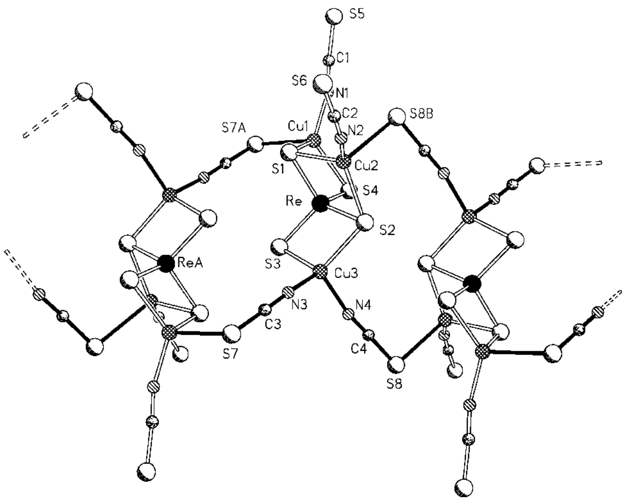

Figure 2. Segment of the anionic chain in **2** showing the alternating 12- and 16-membered rings.

Structure of compound 3: The new type of structure of the discrete anion in **3** with a Cu/Re ratio of 1:1 is shown in Figure 3. It can be formally described as a dimer consisting of two {(ReS$_4$)Cu(NCS)} units with N bonded NCS$^-$ groups and connected by Cu–S bonds, whereby an eight-membered Cu(NCS)Cu(NCS) ring is formed. Until now, such rings have only been found in the polymeric species $\{(WS_4)Cu_3(NCS)_3^{2-}\}_\infty$[11] and $\{(MS_4)Cu_4(NCS)_4^{2-}\}_\infty$ (M = Mo, W).[11, 15, 16]

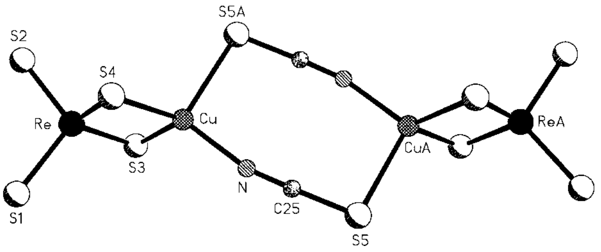

Figure 3. Structure of the discrete anion of **3**.

Spectroscopic results: The presence of an ReS$_4^-$ group can in principle be proven, by measurement of the electronic absorption spectra, according to the presence of bands that are caused by S$\rightarrow$Re charge-transfer interactions.[1a] However, in the case of strong interactions of the ReS$_4^-$ ligand with soft cationic centres like Cu$^+$ or Ag$^+$ the situation is complicated as the related orbitals are perturbed. A characteristic in these cases is the occurrence of bands at lower energies [in the present case for instance at 16.8 (**1**) and 16.5 $\times$ 10^3 cm^{-1} (**2**)], which can be approximately assigned to Cu(3d)$\rightarrow$Re(5d)-type transitions.

In general it is also possible to identify the type of coordination of a thiometalate ligand from the vibrational spectra (see related study in ref. [20]), but in cases of small mechanical coupling as a result of the heavy mass of the relevant 5d transition metal atom, which can lead to accidental degeneracy of the $\tilde{\nu}$(M=S) type vibrations, their usefulness is limited (see also ref. [21]). Still, in the case of compounds **1** and **3**, one or two higher energy bands above 500 cm^{-1} are a clear proof for the presence of one or two terminal Re=S bonds, respectively.

It is also in principle possible (though not easy) to distinguish between bridging (in **1**, **2** and **3**) and terminal NCS ligands (in **2**) and correspondingly between N- or S-coordination. However, the identification of the bands is usually difficult owing to the presence of other bands in the region of the characteristic $\tilde{\nu}$(C=S)- and δ(NCS)-type vibrations and especially due to the weak intensities of the corresponding bands. The $\tilde{\nu}$(CN) frequencies of the stretching modes (the best analytical tool!) are generally lower for N-bonded complexes than for S-bonded complexes and higher in the case of a bridging ligand than in cases of terminal NCS groups. In this context it is important to realize that the band of maximum intensity of **2** with terminal CuNCS groups occurs at lower wavenumbers than the corresponding bands of the other two compounds. A detailed discussion of the criteria that have been developed to distinguish between the different bonding types of the NCS ligand in metal complexes by vibrational spectroscopy is given by Nakamoto.[22]

Conclusion

The ReS$_4^-$ ligand is a powerful synthon for the synthesis of heterometallic coordination compounds, including related low-dimensional solids, and seems to be easier to handle than the higher charged MS$_4^{2-}$ (M = Mo, W) ions as the dimensionality of the products can be more easily planned from the relative amount of reactants (some related information is summarized in Table 4). It is even possible to prepare related compounds through the stepwise capping of the edges of an ReS$_4^-$ tetrahedron with soft cations.[12] In order to understand the different ligand properties of the three above-mentioned thiometalates, it is worthwhile to compare anionic species with the same composition, such as that of **1** and [(MS$_4$)Cu$_2$(NCS)$_2$]$^{2-}$.[15] Whereas **1** forms a one-dimensional anionic species with terminal Re=S bonds, the latter complex represents a discrete unit whereby all four S atoms of the MS$_4^{2-}$-type anion are coordinated to the Cu atoms. The reason for the difference is the smaller charge density on the S atoms of the ReS$_4^-$ ion (favouring a terminal Re=S bond); this is a result of its smaller overall charge as well as to the comparably larger Re–S bond order.[11]

A fascinating aspect of the present type of chemistry is the possibility to study the relations between typical solid-state structures (as in the case of CuNCS), derived solid-state structures (as in **1** and **2**) and even molecular structures (as in **3**). It can be assumed that a careful study of the principles discussed here will enable us in the future in similar chemical situations to prepare compounds deliberately with interesting structural motifs. The thiocyanates are especially suitable for this purpose as the bridging of metal atoms in very different ways is possible, with the consequence that either low-dimensional solids even with the structural motif of the crystalline AgNCS[23] or discrete ring-type species with very different size and shape can been prepared.

Acknowledgments: The financial assistance from the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and a generous gift of Rhenium compounds from the Degussa AG are gratefully acknowledged. M.I. Khan thanks the DAAD for the award of a fellowship and all authors thank F. Peters for his contribution to the section Structure Determination.

Received: July 25, 1997 [F781]

---

[1] a) A. Müller, E. Diemann, R. Jostes, H. Bögge, *Angew. Chem.* **1981**, *93*, 957–977; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 934–955; A. Müller, E. Diemann, *Metallothio Anions*, in *Comprehensive Coordination Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, ch. 16.3, pp. 559–577; C. D. Garner, *Molybdenum: Special Topics*, in *Comprehensive Coordination Chemistry*, *Vol. 3* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, ch. 36.6, pp. 1421–1444; b) A. Müller, E. Diemann, *J. Chem. Soc. Chem. Commun.* **1971**, 65.

[2] a) A. Müller, E. Krickemeyer, H. Bögge, M. Penk, D. Rehder, *Chimia* **1986**, *40*, 50–52; A. Müller, E. Krickemeyer, H. Bögge, *Z. Anorg. Allg. Chem.* **1987**, *554*, 61–78; b) A. Müller, E. Krickemeyer, F.-W. Baumann, R. Jostes, H. Bögge, *Chimia* **1986**, *40*, 310–311; A. Müller, E. Krickemeyer, H. Bögge, *Angew. Chem.* **1986**, *98*, 987; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 990–991; C. D. Scattergood, C. D. Garner, W. Clegg, *Inorg. Chim. Acta* **1987**, *132*, 161–162; A. Müller, R. Jostes, E. Krickemeyer, H. Bögge, *Naturwissenschaften* **1987**, *74*, 388–389; A. Müller, R. Jostes, K. Schmitz, E. Krickemeyer, H. Bögge, E. Bill, A. Trautwein, *Inorg. Chim. Acta* **1988**, *149*, 9–12; A. Müller, E. Krickemeyer, H. Bögge, M. Penk, *Chimia* **1989**, *43*, 319–320; S. Ciurli, M. J. Carney, R. H. Holm, G. C. Papaefthymiou, *Inorg. Chem.* **1989**, *28*, 2696–2698; K. E. Howard, J. R. Lockemeyer, M. A. Massa, T. B. Rauchfuss, S. R. Wilson, X. Yang, *Inorg. Chem.* **1990**, *29*, 4385–4390; S. Ciurli, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 743–750; R. Schäfer, W. Kaim, J. Fiedler, *Inorg. Chem.* **1993**, *32*, 3199–3200.

[3] S. C. Lee, R. H. Holm, *J. Am. Chem. Soc.* **1990**, *112*, 9654–9655; S. C. Lee, J. Li, J. C. Mitchell, R. H. Holm, *Inorg. Chem.* **1992**, *31*, 4333–4338; C. D. Scattergood, P. G. Bonney, J. M. Slater, C. D. Garner, W. Clegg, *J. Chem. Soc. Chem. Commun.* **1987**, 1749–1750.

[4] W. P. Binnie, M. J. Redman, W. J. Mallio, *Inorg. Chem.* **1970**, *9*, 1449–1452; A. Müller, R. Menge, *Z. Anorg. Allg. Chem.* **1972**, *393*, 259–265.

[5] For related remarks referring to MS$_4^{2-}$ (M = Mo, W) anions see also Y. Jeannin, F. Sécheresse, S. Bernès, F. Robert, *Inorg. Chim. Acta* **1992**, *198–200*, 493–505.

[6] A. Müller, E. Diemann, V. V. K. Rao, *Chem. Ber.* **1970**, *103*, 2961–2971.

[7] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101977 (**3**) CCDC-101978 (**1**) CCDC-101979 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] SHELXTL-PLUS, Revision 3.4, Siemens Analytical X-ray Instruments, **1988**.

[9] M. Kabesova, M. Dunaj-Jurco, M. Serator, J. Gazo, J. Garaj, *Inorg. Chim. Acta* **1978**, *17*, 161–165.

[10] A. Müller, M. Dartmann, C. Römer, W. Clegg, G. M. Sheldrick, *Angew. Chem.* **1981**, *93*, 1118–1119; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 1060–1061.

[11] J.-M. Manoli, C. Potvin, F. Sécheresse, S. Marzak, *Inorg. Chim. Acta* **1988**, *150*, 257–268. It should be mentioned that it is also possible to generate 8-, 12-, 16- and 24-membered ring systems by linking CuI$_4$ and AgI$_4$ tetrahedra (H. Krautscheid, *Habilitationsschrift*, Karlsruhe, **1996**; L.-N. Rudolph, H. Hartl, *Z. Anorg. Allg. Chem.* **1997**, *623*, 687–694).

[12] A. Müller, E. Krickemeyer, A. Hildebrand, H. Bögge, K. Schneider, M. Lemke, *J. Chem. Soc. Chem. Commun.* **1991**, 1685–1687.

[13] R. J. H. Clark, S. Joss, M. Zvagulis, C. D. Garner, J. R. Nicholson, *J. Chem. Soc. Dalton Trans.* **1986**, 1595–1601, and references therein; F. Sécheresse, F. Robert, S. Marzak, J.-M. Manoli, C. Potvin, *Inorg. Chim. Acta* **1991**, *182*, 221–228.

[14] J. R. Nicholson, A. C. Flood, C. D. Garner, W. Clegg, *J. Chem. Soc. Chem. Commun.* **1983**, 1179–1180.

[15] C. Potvin, J.-M. Manoli, F. Sécheresse, S. Marzak, *Inorg. Chem.* **1987**, *26*, 4370–4374.

[16] J.-M. Manoli, C. Potvin, F. Sécheresse, S. Marzak, *J. Chem. Soc. Chem. Commun*. **1986**, 1557–1558.

[17] F. Sécheresse, S. Bernès, F. Robert, Y. Jeannin, *J. Chem. Soc. Dalton Trans.* **1991**, 2875–2881.

[18] A. Müller, E. Krickemeyer, M. Penk, *J. Chem. Soc. Chem. Commun.* **1990**, 321–322.

[19] A. Müller, U. Schimanski, J. Schimanski, *Inorg. Chim. Acta* **1983**, *76*, L245–L246.

[20] A. Müller, W. Jaegermann, W. Hellmann, *J. Mol. Struct.* **1983**, *100*, 559–570; A. Müller, W. Hellmann, *Spectrochim. Acta A* **1985**, *41*, 359–366.

[21] N. Weinstock, H. Schulze, A. Müller, *J. Chem. Phys.* **1973**, *59*, 5063–5067.

[22] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, Wiley, New York, **1997**, pp. 116–121.

[23] I. Lindqvist, *Acta Crystallogr.* **1957**, *10*, 29–32.