of the intramusculary transplanted sarcoma 180 tumor, ICR was not given at the site of the tumor, as in the P 388 and Walker 256 tumor model, which are so-called "ip-ip" models, but it was applied intravenously in order to treat a tumor growing in solid form in the left hind leg of the animal. Such models are necessary to evaluate the systemic effect of a compound. Prerequisite for this is an appropriate galenic formulation or a water-soluble compound that is stable enough against hydrolysis during dissolution and treatment, as is the case with our ruthenium compound ICR. The ip-ip models do not take the systemic effect into account, because the drug is applied at the site of the tumor. This is why such additional models are necessary, where a solid tumor is treated by intravenous application, in order to evaluate the systemic effect of a substance that is indispensable for a sufficient cancer therapy. Toxicity in terms of body weight change was tolerable in all three models. From a preliminary P 388 screen it could be concluded that the three methyl-substituted derivatives are less active than the unsubstituted compound. The *T*/*C* values obtained were in the range between 130% and 150%. Higher values may be possible by further evaluation of the optimum dose and dose schedule.

The reported activity against the transplantable tumor models described above indicates tumor-inhibiting properties in general, but it cannot guarantee activity of the test compound against specific human organ tumors. Within the range of human tumors, gastrointestinal cancers are one of the major causes of cancer mortality in the western world. No really sufficient chemotherapy against this type of tumors could be established until now. Due to this fact, the title compound, imidazolium *trans*-bis(imidazole)tetrachlororuthenate(III) (ICR), was tested by Garzon et al.[16] against autochthonous colorectal tumors in rats, which are highly predictive for the clinical situation in humans. In this model, promising effects of this compound were observed.

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Registry No. 1, 103875-27-0; **2**, 111137-62-3; 2-MeImH[*trans*-Ru(2-MeIm)$_2$Cl$_4$], 111137-60-1; 1-MeImH[*trans*-Ru(1-MeIm)$_2$Cl$_4$], 111026-31-4.

Supplementary Material Available: Tables of anisotropic thermal parameters (3 pages); listings of structure factors (22 pages). Ordering information is given on any current masthead page.

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(16) Garzon, F. T.; Berger, M. R.; Keppler, B. K.; Schmähl, D. *Cancer Chemother. Pharmacol.* **1987**, *19*, 347–349.

Contribution from the Laboratoire de Cinétique Chimique, Université Pierre et Marie Curie, 1 Rue Guy de la Brosse, 75005 Paris, France, and Laboratoire de Chimie des Metaux de Transition and Laboratoire de Chimie des Polymères Inorganiques, Université Pierre et Marie Curie, 8 Rue Cuvier, 75252 Paris Cedex 05, France

Heterobimetallic Complexes of Copper(I) with Thiotungstates and Thiomolybdates. Synthesis and Structural Characterization of $(PPh_4)_2[(CuNCS)_2WS_4]$ and of Polymeric $(PPh_4)_2[(CuNCS)_4WS_4]$

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Reaction of $(PPh_4)_2MS_4$ (M = Mo, W) with CuCl and KSCN or CuNCS in acetone or acetonitrile affords a new set of mixed metal–sulfur compounds: discrete $[(CuNCS)_2MS_4]^{2-}$ and polymeric $[(CuNCS)_4MS_4]^{2-}$ dianions. $(PPh_4)_2[(CuNCS)_2WS_4]$ crystallizes in monoclinic space group $P2_1/c$ with $a = 32.89$ (2) Å, $b = 9.312$ (4) Å, $c = 17.993$ (5) Å, $\beta = 113.11$ (4)°, and $Z = 4$. Least-squares refinement of 328 variables led to a value of the conventional R index (on F) of 0.053 and an R_w value of 0.049 for 3770 reflections with $I > 3.0\sigma(I)$. The crystal structure of $(PPh_4)_2[(CuNCS)_2WS_4]$ (**1**) reveals the presence of discrete, almost linear trinuclear dianions and involves the coordination of a slightly distorted tetrahedral WS_4 moiety to two copper(I) atoms with each trigonal copper(I) atom also participating in Cu–NCS bond lengths of 1.87 (1) and 1.85 (1) Å. This structure contrasts with the polymeric nature of $(PPh_4)_2[(CuNCS)_4WS_4]$ (**3**), which crystallizes in monoclinic space group $P2_1/n$ with $a = 22.641$ (9) Å, $b = 18.044$ (4) Å, $c = 14.439$ (5) Å, $\beta = 96.22$ (4)°, and $Z = 4$. Least-squares refinement of 400 variables led to a value of the conventional R index (on F) of 0.050 for 6590 reflections with $I > 3.0\sigma(I)$. The crystal structure determination shows that four edges of the tetrahedral WS_4 core are bridged by Cu(I) atoms, giving an aggregate of approximate D_{2d} symmetry with NCS bridges linking different aggregates via two mutually cis pseudotetrahedral coppers to form an infinite zigzag chain running about the 2_1 axis. One of the remaining two copper atoms adopts a trigonal-planar environment as in **1**, while the other copper atom assumes a geometry intermediate between tetrahedral (short nonbonded distance Cu(3)···S(3) = 3.042 (4) Å) and trigonal planar. These weak interactions between copper and the sulfur atom S(3) of a NCS group lead to a two-dimensional-network polymer parallel to the (101) plane. The electronic spectra of the complexes are dominated by the internal transitions of the MS_4^{2-} ligand modified by additional CuNCS units. The structural data have been used to interpret vibrational spectroscopic data of the thiocyanate groups.

The tetrathiometalates MS_4^{2-} (M = Mo, W) have been studied for their ability to coordinate to transition metals[1] and particularly to Cu in connection with the possible relevance of Cu–Mo biological antagonism.[2] The neutral species CuX (X = CN,[3] Cl[4]) coordinate to MS_4^{2-} to form aggregates in which MS_4^{2-} acts as a bi- or tridentate ligand. Other interesting clusters include species stabilized in polymeric form such as $(PPh_4)_2[(CuBr)_4MoS_4]$[5] and $(NMe_4)_2[(CuNCS)_4WS_4]$[6] with MS_4^{2-} acting as a tetradentate ligand. Taking advantage of the fact that nonchelating ambidentate ligands such as CN^- and NCS^- are capable of bridging metal nuclei to form different polymeric anionic compounds, we have expanded our studies on the MS_4^{2-}/CuNCS system. We report herein the synthesis and characterization of the tetra-

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(1) Müller, A.; Diemann, E.; Jostes, R., Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934 and references therein.

(2) Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* **1984**, *59*, 239.

(3) (a) Müller, A.; Dartmann, M.; Römer, C.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *20*, 1060. (b) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519.

(4) (a) Manoli, J. M.; Potvin, C.; Sécheresse, F. *J. Chem. Soc., Chem. Commun.* **1982**, 1159. (b) Clegg, W.; Garner, C. D.; Nicholson, J. R. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 552. (c) Potvin, C.; Manoli, J. M.; Salis, M.; Sécheresse, F. *Inorg. Chim. Acta* **1984**, *83*, L19. (d) Sécheresse, F.; Salis, M.; Potvin, C.; Manoli, J. M. *Inorg. Chim. Acta* **1986**, *114*, L19.

(5) Nicholson, J. R.; Flood, A. C.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1179.

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Table I. Crystal Data, Data Collection, and Refinement of the Structures

	1	**3**
formula	$C_{50}H_{40}P_2N_2Cu_2WS_6$	$C_{52}H_{40}P_2N_4Cu_4WS_8$
mol wt	1234	1477
a, Å	32.89 (2)	22.641 (9)
b, Å	9.312 (4)	18.044 (4)
c, Å	17.993 (5)	14.439 (5)
β, deg	113.11 (4)	96.22 (4)
V, Å^3	5069.5	5864.1
space group	$P2_1/c$	$P2_1/n$
Z	4	4
T of data collecn, K	293	293
radiation (monochromated)	Mo Kα (λ = 0.71069 Å)	Cu Kα (λ = 1.54178 Å)
crystal dimens, mm	0.08 × 0.12 × 0.23	0.12 × 0.20 × 0.20
linear abs coeff, cm^{-1}	32.9 (Mo Kα)	87.2 (Cu Kα)
transmission factors	0.81–0.89	0.49–0.65
scan range, 2θ, deg	4–50	4–120
scan rate, deg min^{-1}	0.9	1.2
scan width, deg	0.7	1.95
stds (measd every 1 h)	606; 12, 0, 0; $\bar{6}0\bar{6}$	044; $0\bar{4}4$; $\bar{5}1\bar{1}$
no. of reflcns measd	7448 ($\pm h,+k,+l$)	8705 ($\pm h,+k,+l$)
no. of data used ($F_o^2 > 3\sigma(F_o^2)$)	3770	6590
no. of variables refined	328	400
R^a	0.053	0.050
R_w	0.049	0.050
GOF	3.59	4.38

[a] The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 4F_0^2/\sigma^2(F_0^2)$. The unweighted and weighted residuals are defined as follows: $R = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

phenylphosphonium salts of the discrete $[(CuNCS)_2MS_4]^{2-}$ and of the polymeric $[(CuNCS)_4MS_4]^{2-}$ dianions.

Experimental Section

All manipulations were carried out in air. Chemicals were used as purchased. Elemental analyses were performed by the "Service Central d'Analyses du CNRS". Infrared spectra (KBr and polyethylene pellets) were recorded on a Perkin-Elmer 580B spectrophotometer. Electronic spectra were obtained on a Kontron 810 spectrophotometer in DMF solution between 600 and 200 nm.

$(PPh_4)_2[(CuNCS)_2WS_4]$ (1). A 0.990-g (1-mmol) amount of $(PPh_4)_2WS_4$ was suspended in 200 mL of acetone. After addition of 0.182 g (1.5 mmol) of CuNCS the mixture was stirred for 30 min at ambient temperature and the yellow precipitate immediately formed was eliminated. The filtrate was concentrated to ca. 100 mL on a rotary evaporator. To this solution was added 100 mL of a 1:2 acetone/heptane mixture to incipient crystallization, and subsequent standing (2 h) at room temperature gave 0.36 g of **1** as yellow crystals. Anal. Calcd (Found): C, 48.66 (47.34); N, 2.27 (2.25); S, 15.57 (15.55); Cu, 10.30 (10.35); W, 14.92 (13.67).

$(PPh_4)_2[(CuNCS)_2MoS_4]$ (2). To a suspension of 0.456 g (0.5 mmol) of $(PPh_4)_2MoS_4$ in 100 mL of acetone were added 0.075 g (0.75 mmol) of CuCl and 0.057 g (0.75 mmol) of NH_4NCS. The mixture was stirred for ca. 30 min and then filtered. The filtrate was reduced to 50 mL on a rotary evaporator, and a mixture of 50 mL of 1:2 acetone/heptane was added. Within 3 h a red-violet precipitate deposited, which was eliminated. The filtrate was allowed to stand at room temperature for an additional 24 h; 0.070 g of red-violet well-shaped crystals was obtained. Anal. Calcd (Found): C, 52.40 (52.40); P, 5.41 (5.69); N, 2.44 (2.32); S, 16.77 (16.46); Cu, 11.09 (10.94); Mo, 8.38 (8.66).

$(PPh_4)_2[(CuNCS)_4WS_4]$ (3). To a solution of 0.245 g (0.25 mmol) of $(PPh_4)_2WS_4$ in acetonitrile (25 mL) were added CuCl (0.100 g, 1 mmol) andd KSCN (0.097 g, 1 mmol). The mixture was stirred for 30 min, and the orange precipitate formed was removed by filtration. The filtrate was reduced to ca. 10 mL by rapid evaporation under vacuum. Addition of 20 mL of ether to the reduced solution followed by cooling at 0 °C (for 24 h) gave 0.040 g of orange microcrystals. Anal. Calcd (Found): C, 42.28 (40.94); N, 3.79 (3.54); S, 17.34 (18.02); Cu, 17.21 (16.19); W, 12.47 (12.37). Well-shaped crystals of **3** suitable for X-ray diffraction experiments were obtained by allowing the filtrate to stand 1 week at 0 °C.

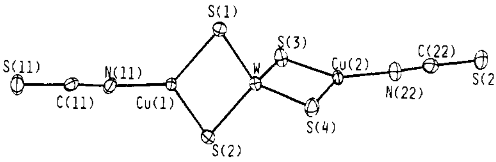

Figure 1. Perspective view (50% ellipsoids) of the $[(CuNCS)_2WS_4]^{2-}$ dianion and the atomic numbering scheme employed.

$(PPh_4)_2[(CuNCS)_4MoS_4]$ (4) was similarly prepared by starting with $(PPh_4)_2MoS_4$. Red-brown crystals (0.035 g) were obtained by slow diffusion of ether in the acetonitrile filtrate within 12 h at ca. 0 °C. Anal. Calcd (Found): C, 44.95 (44.99); N, 4.03 (3.97); S, 18.45 (18.02); Cu, 18.30 (17.75); Mo, 6.91 (7.40).

Crystal Structure Determination. Crystals of **1** and **3** were selected for X-ray experiments. Preliminary Weissenberg photographs established the monoclinic symmetry for both compounds. Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized radiation and a θ–2θ flying-step-scan technique. Cell data and specific parameters pertaining to the data collections are reported in Table I. The intensities were corrected for polarization and Lorentz effects. Absorption corrections have been carried out for both compounds by using the Gaussian integration method of Ibers' AGNOST[7] program. Both structures were solved by the heavy-atom method. Three-dimensional Patterson maps revealed the position of the tungsten atoms. Successive least-squares refinements and difference Fourier calculations revealed the positions of the remaining atoms. Anisotropic temperature factors were introduced for the W, Cu, S, P, N, and C (of the anions) atoms and isotropic thermal parameters for the C atoms of the PPh_4 cations. Riding isotropic hydrogen atoms were included in the refinements subject to the constraint C–H = 1.08 Å and U(H) = 1.1U(C), where U(C) is the equivalent isotropic thermal parameter of a carbon atom of the phenyl ring. Final agreement indices are given in Table I. Neutral atom scattering factors with anomalous dispersion corrections were used.[8] All computations were performed by using SHELX 76 on a Gould Concept 32/87 computer. Final atomic positional parameters are presented in Tables II and III. Bond distances and angles within the two anions are found in Table IV.

Results and Discussion

Crystal Structure. The crystal structure of **1** consists of a discrete complex anion (Figure 1) and of PPh_4 cations. The molecular structure of the $[(CuNCS)_2WS_4]^{2-}$ anion is closely related to that of $[(CuCN)_2MoS_4]^{2-}$ [3b] and of $[(CuCl)_2WS_4]^{2-}$.[4d] In each anion the copper and the tungsten atoms have respectively a trigonal planar and a slightly distorted tetrahedral coordination geometry. The copper atom lies (to within 0.035 Å) in the plane of two sulfur atoms and one nitrogen atom. The WS_2CuN moieties are planar (maximum deviation 0.043 Å) with Cu–S distances slightly shorter than those observed in $[(CuCl)_2WS_4]^{2-}$.[4d] As expected, the thiocyanate groups are nearly linear while the Cu–N–C angles are almost linear and lie within the range usually reported for N-bonded terminal NCS groups.

The structure of **3** consists of one crystallographically independent $[(CuNCS)_4WS_4]^{2-}$ anion (result confirming the chemical analysis for the Cu:W ratio) and two PPh_4 cations. Four edges of the WS_4 tetrahedron are bridged by copper atoms with W···Cu distances ranging from 2.616 (2) to 2.643 (2) Å. The Cu···W···Cu angles (166.33 (6) and 170.20 (5)°) concerning the two mutually trans copper atoms lead to an approximate D_{2d} symmetry for the WS_4Cu_4 aggregate. Two cis copper atoms, Cu(1) and Cu(2), have a distorted-tetrahedral geometry with their tetrahedral apices occupied by two bridging sulfur atoms and one nitrogen and one sulfur atom of two different non symmetrically related NCS groups, forming a CuS_3N unit. The corresponding NCS ligands are involved in interaggregate bridges between copper atoms of the next WS_4Cu_4 unit, forming an infinite zigzag chain running along the 2_1 axis (Figure 2). In description of the distortion of the coordination sphere from different geometries one additional

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(6) Manoli, J. M.; Potvin, C.; Sécheresse, F.; Marzak, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1557.

(7) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

(8) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

Table II. Atom Coordinates for $[P(C_6H_5)_4]_2[(CuNCS)_2WS_4]$ (**1**)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	0.75112 (2)	0.53158 (6)	0.49975 (4)	C(136)	0.4493 (4)	−0.163 (1)	0.4582 (8)
Cu(1)	0.66745 (5)	0.6054 (2)	0.44433 (9)	C(141)	0.3939 (4)	0.206 (1)	0.3497 (7)
Cu(2)	0.83493 (5)	0.4622 (2)	0.5469 (1)	C(142)	0.3929 (4)	0.248 (2)	0.2768 (8)
S(1)	0.7146 (1)	0.6478 (4)	0.3863 (2)	C(143)	0.3992 (4)	0.393 (2)	0.2645 (9)
S(2)	0.7047 (1)	0.4908 (4)	0.5582 (2)	C(144)	0.4064 (4)	0.493 (2)	0.3222 (8)
S(3)	0.7772 (1)	0.3280 (4)	0.4735 (2)	C(145)	0.4067 (5)	0.452 (2)	0.396 (1)
S(4)	0.8077 (1)	0.6608 (4)	0.5777 (2)	C(146)	0.4003 (5)	0.306 (2)	0.409 (1)
S(11)	0.5162 (1)	0.6335 (5)	0.3427 (3)	C(211)	0.1291 (4)	0.288 (1)	0.6038 (7)
S(22)	0.9836 (1)	0.3854 (7)	0.6177 (3)	C(212)	0.0893 (4)	0.357 (1)	0.5892 (7)
N(11)	0.6073 (3)	0.648 (1)	0.4057 (6)	C(213)	0.0887 (4)	0.500 (1)	0.6047 (8)
C(11)	0.5686 (4)	0.640 (1)	0.3775 (7)	C(214)	0.1271 (4)	0.579 (2)	0.6354 (8)
N(22)	0.8941 (3)	0.421 (1)	0.5768 (7)	C(215)	0.1673 (5)	0.512 (1)	0.6525 (8)
C(22)	0.9316 (5)	0.407 (2)	0.5927 (8)	C(216)	0.1680 (4)	0.366 (1)	0.6353 (7)
P(1)	0.3823 (1)	0.0250 (4)	0.3664 (2)	C(221)	0.1818 (4)	0.025 (1)	0.6337 (7)
P(2)	0.1283 (1)	0.1044 (4)	0.5780 (2)	C(222)	0.2156 (4)	0.054 (1)	0.6097 (8)
C(111)	0.3306 (4)	0.023 (1)	0.3748 (7)	C(223)	0.2596 (5)	0.008 (2)	0.6583 (9)
C(112)	0.3197 (4)	−0.093 (1)	0.4135 (7)	C(224)	0.2632 (5)	−0.072 (2)	0.7234 (9)
C(113)	0.2781 (4)	−0.095 (2)	0.4191 (8)	C(225)	0.2307 (5)	−0.104 (2)	0.7477 (9)
C(114)	0.2499 (5)	0.013 (2)	0.3856 (8)	C(226)	0.1880 (5)	−0.055 (1)	0.7016 (8)
C(115)	0.2590 (4)	0.126 (2)	0.3462 (8)	C(231)	0.0875 (4)	0.014 (1)	0.6043 (8)
C(116)	0.2999 (4)	0.130 (1)	0.3402 (7)	C(232)	0.0605 (4)	−0.086 (1)	0.5539 (8)
C(121)	0.3810 (4)	−0.081 (1)	0.2825 (6)	C(233)	0.0307 (4)	−0.159 (1)	0.5800 (8)
C(122)	0.4187 (4)	−0.092 (1)	0.2674 (7)	C(234)	0.0306 (5)	−0.130 (2)	0.6527 (9)
C(123)	0.4182 (4)	−0.170 (1)	0.2013 (7)	C(235)	0.0571 (5)	−0.030 (2)	0.703 (1)
C(124)	0.3793 (4)	−0.234 (1)	0.1521 (7)	C(236)	0.0864 (5)	0.044 (2)	0.6790 (9)
C(125)	0.3425 (4)	−0.226 (1)	0.1675 (7)	C(241)	0.1146 (4)	0.083 (1)	0.4720 (7)
C(126)	0.3420 (4)	−0.148 (1)	0.2323 (7)	C(242)	0.0910 (4)	0.191 (1)	0.4175 (7)
C(131)	0.4228 (4)	−0.047 (1)	0.4587 (7)	C(243)	0.0788 (4)	0.164 (2)	0.3355 (8)
C(132)	0.4284 (4)	0.014 (1)	0.5314 (8)	C(244)	0.0897 (5)	0.042 (2)	0.311 (1)
C(133)	0.4588 (4)	−0.044 (1)	0.6035 (8)	C(245)	0.1122 (5)	−0.063 (2)	0.361 (1)
C(134)	0.4827 (4)	−0.159 (1)	0.6018 (8)	C(246)	0.1260 (4)	−0.041 (2)	0.4441 (9)
C(135)	0.4785 (4)	−0.220 (2)	0.5322 (9)				

Table III. Atomic Coordinates for $[P(C_6H_5)_4]_2[(CuNCS)_4WS_4]$ (**3**)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	0.34054 (2)	0.37607 (2)	0.66643 (3)	C(132)	0.4959 (5)	−0.0038 (6)	0.1912 (7)
Cu(1)	0.28621 (7)	0.26028 (8)	0.7307 (1)	C(133)	0.4931 (5)	−0.0694 (7)	0.2419 (8)
Cu(2)	0.29283 (6)	0.49023 (7)	0.7453 (1)	C(134)	0.5429 (5)	−0.0966 (7)	0.2910 (8)
Cu(3)	0.41069 (9)	0.4679 (1)	0.5739 (1)	C(135)	0.5972 (6)	−0.0628 (7)	0.2915 (8)
Cu(4)	0.3809 (1)	0.2735 (1)	0.5612 (1)	C(136)	0.6016 (5)	0.0027 (6)	0.2414 (7)
S(34)	0.3374 (1)	0.3809 (2)	0.5115 (2)	C(141)	0.4804 (4)	0.1508 (5)	0.0922 (6)
S(12)	0.2477 (1)	0.3779 (1)	0.7046 (2)	C(142)	0.4604 (4)	0.1353 (6)	−0.0002 (7)
S(14)	0.3859 (1)	0.2716 (1)	0.7183 (2)	C(143)	0.4031 (5)	0.1578 (6)	−0.0347 (8)
S(23)	0.3920 (1)	0.4725 (1)	0.7300 (2)	C(144)	0.3686 (5)	0.1943 (7)	0.0198 (8)
S(1)	0.2417 (1)	0.0603 (1)	0.9091 (2)	C(145)	0.3879 (6)	0.2095 (8)	0.112 (1)
S(2)	0.2566 (2)	0.6956 (1)	0.9205 (2)	C(146)	0.4458 (5)	0.1874 (7)	0.1481 (9)
S(3)	0.4930 (1)	0.6375 (2)	0.3973 (2)	C(211)	0.7971 (4)	0.0261 (6)	0.5673 (7)
S(4)	0.4099 (3)	0.0822 (3)	0.3630 (4)	C(212)	0.8151 (5)	0.0857 ()	0.5178 (7)
N(1)	0.2684 (4)	0.1934 (5)	0.8242 (6)	C(213)	0.7725 (6)	0.1263 (8)	0.4591 (9)
C(1)	0.2572 (4)	0.1381 (5)	0.8595 (6)	C(214)	0.7150 (6)	0.1030 (8)	0.456 (1)
N(2)	0.2723 (3)	0.5595 (4)	0.8350 (5)	C(215)	0.6962 (7)	0.0459 (8)	0.504 (1)
C(2)	0.2652 (4)	0.6149 (5)	0.8712 (6)	C(216)	0.7377 (5)	0.0048 (7)	0.5627 (8)
N(3)	0.4316 (4)	0.5430 (6)	0.5015 (7)	C(221)	0.8201 (4)	−0.0870 (5)	0.7162 (7)
C(3)	0.4566 (4)	0.5832 (6)	0.4588 (7)	C(222)	0.7937 (5)	−0.1500 (6)	0.6711 (9)
N(4)	0.4015 (6)	0.1973 (6)	0.4841 (7)	C(223)	0.7699 (6)	−0.2046 (8)	0.724 (1)
C(4)	0.4041 (6)	0.1491 (7)	0.4338 (9)	C(224)	0.7719 (6)	−0.1962 (9)	0.819 (1)
P(1)	0.5542 (1)	0.1218 (1)	0.1391 (2)	C(225)	0.7972 (6)	−0.1343 (8)	0.864 (1)
P(2)	0.8525 (1)	−0.0200 (1)	0.6456 (2)	C(226)	0.8210 (5)	−0.0792 (7)	0.8105 (8)
C(111)	0.5801 (4)	0.1861 (6)	0.2311 (7)	C(231)	0.8886 (4)	0.0510 (5)	0.7188 (7)
C(112)	0.6106 (5)	0.2498 (6)	0.2085 (8)	C(232)	0.8550 (5)	0.1090 (5)	0.7470 (7)
C(113)	0.6235 (5)	0.3023 (7)	0.2802 (8)	C(233)	0.8815 (4)	0.1640 (6)	0.8044 (7)
C(114)	0.6085 (5)	0.2899 (7)	0.3640 (8)	C(234)	0.9414 (4)	0.1603 (6)	0.8330 (7)
C(115)	0.5791 (5)	0.2275 (7)	0.3889 (9)	C(235)	0.9745 (5)	0.1029 (6)	0.8043 (7)
C(116)	0.5646 (5)	0.1739 (6)	0.3175 (7)	C(236)	0.9490 (4)	0.0477 (6)	0.7484 (7)
C(121)	0.5984 (4)	0.1204 (6)	0.0456 (7)	C(241)	0.9056 (4)	−0.0669 (5)	0.5827 (7)
C(122)	0.6306 (5)	0.0580 (7)	0.0247 (8)	C(242)	0.9085 (4)	−0.0558 (6)	0.4894 (7)
C(123)	0.6618 (6)	0.0595 (8)	−0.0531 (9)	C(243)	0.9525 (5)	−0.0919 (6)	0.4436 (8)
C(124)	0.6624 (6)	0.1178 (8)	−0.110 (1)	C(244)	0.9935 (5)	−0.1352 (7)	0.4945 (8)
C(125)	0.6293 (6)	0.1809 (8)	−0.089 (1)	C(245)	0.9910 (5)	−0.1465 (6)	0.5868 (8)
C(126)	0.5989 (5)	0.1808 (7)	−0.0138 (8)	C(246)	0.9472 (4)	−0.1137 (6)	0.6330 (7)
C(131)	0.5502 (4)	0.0329 (5)	0.1925 (7)				

factor has to be considered, this being the distance of the copper from the bounding faces of the polyhedron. Those distances for the four different copper atoms of **3** and the two copper atoms of **1** are listed in the supplementary material. The coordination geometry about Cu(4) is trigonal planar with angles about Cu(4) (sum of angles subtended by Cu(4) 359.7°) similar to the corresponding angles reported in $[(CuNCS)_2WS_4]^{2-}$. Inspection of the Cu(3) coordination geometry shows a short nonbonded cop-

Table IV. Interatomic Distances (Å) and Selected Angles (deg) for $[(CuNCS)_2WS_4]^{2-}$ (Anion of **1**) and $[(CuNCS)_4WS_4]^{2-}$ (Anion of **3**)[a]

	Compound **1**		
W–S(1)	2.203 (3)	W–S(3)	2.207 (4)
W–S(2)	2.201 (4)	W–S(4)	2.198 (3)
W···Cu(1)	2.624 (2)	W···Cu(2)	2.627 (2)
Cu(1)–S(1)	2.219 (5)	Cu(2)–S(3)	2.224 (4)
Cu(1)–S(2)	2.206 (4)	Cu(2)–S(4)	2.218 (4)
Cu(1)–N(11)	1.87 (1)	Cu(2)–N(22)	1.85 (1)
N(11)–C(11)	1.17 (2)	N(22)–C(22)	1.16 (2)
C(11)–S(11)	1.59 (1)	C(22)–S(22)	1.60 (2)
S(1)–W–S(2)	107.4 (1)	S(2)–W–S(3)	110.8 (2)
S(1)–W–S(3)	109.9 (1)	S(2)–W–S(4)	111.2 (1)
S(1)–W–S(4)	109.8 (1)	S(3)–W–S(4)	107.7 (1)
Cu(1)···W···Cu(2)	176.61 (8)		
S(1)–Cu(1)–S(2)	106.7 (1)	S(3)–Cu(2)–S(4)	106.4 (1)
S(1)–Cu(1)–N(11)	128.5 (4)	S(3)–Cu(2)–N(22)	127.8 (4)
S(2)–Cu(1)–N(11)	124.8 (4)	S(4)–Cu(2)–N(22)	125.8 (4)
W–S(1)–Cu(1)	72.8 (1)	W–S(3)–Cu(2)	72.7 (1)
W–S(2)–Cu(1)	73.1 (1)	W–S(4)–Cu(2)	73.0 (1)
Cu(1)–N(11)–C(11)	164 (1)	Cu(2)–N(22)–C(22)	174 (1)
N(11)–C(11)–S(11)	177 (1)	N(22)–C(22)–S(22)	178 (1)
	Compound **3**		
W–S(12)	2.229 (2)	W–S(23)	2.235 (2)
W–S(14)	2.237 (3)	W–S(34)	2.232 (3)
W···Cu(1)	2.643 (2)	W···Cu(3)	2.616 (2)
W···Cu(2)	2.641 (1)	W···Cu(4)	2.620 (2)
Cu(1)–S(12)	2.310 (3)	Cu(2)–S(12)	2.316 (3)
Cu(1)–S(14)	2.293 (3)	Cu(2)–S(23)	2.302 (3)
Cu(1)–S(2)^{i}	2.569 (3)	Cu(2)–S(1)^{ii}	2.608 (3)
Cu(1)–N(1)	1.887 (9)	Cu(2)–N(2)	1.893 (8)
N(1)–C(1)	1.16 (1)	N(2)–C(2)	1.15 (1)
C(1)–S(1)	1.63 (1)	C(2)–S(2)	1.64 (1)
Cu(3)–S(23)	2.290 (3)	Cu(4)–S(14)	2.259 (3)
Cu(3)–S(34)	2.260 (3)	Cu(4)–S(34)	2.255 (4)
Cu(3)–S(3)^{iii}	3.042 (4)		
Cu(3)–N(3)	1.88 (1)	Cu(4)–N(4)	1.86 (1)
N(3)–C(3)	1.14 (1)	N(4)–C(4)	1.14 (2)
C(3)–S(3)	1.61 (1)	C(4)–S(4)	1.60 (1)
S(12)–W–S(14)	109.9 (1)	S(23)–W–S(34)	109.9 (1)
S(12)–W–S(23)	110.5 (1)	S(14)–W–S(23)	108.6 (1)
S(12)–W–S(34)	108.6 (1)	S(14)–W–S(34)	109.4 (1)
Cu(1)···W···Cu(2)	103.74 (5)	Cu(2)···W···Cu(3)	89.45 (6)
Cu(1)···W···Cu(3)	166.33 (6)	Cu(2)···W···Cu(4)	170.20 (5)
Cu(1)···W···Cu(4)	81.39 (7)	Cu(3)···W···Cu(4)	85.05 (7)
S(12)–Cu(1)–S(14)	105.2 (1)	S(12)–Cu(2)–S(23)	105.2 (1)
N(1)–Cu(1)–S(14)	113.6 (3)	N(2)–Cu(2)–S(12)	128.1 (3)
N(1)–Cu(1)–S(12)	126.8 (3)	N(2)–Cu(2)–S(23)	118.1 (2)
N(1)–Cu(1)–S(2)^{i}	103.1 (3)	S(12)–Cu(2)–S(1)^{ii}	97.1 (1)
S(14)–Cu(1)–S(2)^{i}	104.9 (1)	S(23)–Cu(2)–S(1)^{ii}	101.0 (1)
S(12)–Cu(1)–S(2)^{i}	100.2 (1)	N(2)–Cu(2)–S(1)^{ii}	101.0 (2)
S(23)–Cu(3)–S(34)	106.9 (1)	S(14)–Cu(4)–S(34)	107.8 (1)
N(3)–Cu(3)–S(23)	126.8 (3)	N(4)–Cu(4)–S(14)	126.9 (4)
N(3)–Cu(3)–S(34)	122.3 (3)	N(4)–Cu(4)–S(34)	125.0 (4)
S(23)–Cu(3)–S(3)^{iii}	92.6 (1)	S(34)–Cu(3)–S(3)^{iii}	94.7 (1)
N(3)–Cu(3)S(3)^{iii}	101.6 (3)		
W–S(12)–Cu(1)	71.20 (8)	W–S(23)–Cu(2)	71.18 (8)
W–S(12)–Cu(2)	71.00 (7)	W–S(23)–Cu(3)	70.65 (9)
W–S(14)–Cu(1)	71.39 (9)	W–S(34)–Cu(3)	71.25 (9)
W–S(14)–Cu(4)	71.3 (1)	W–S(34)–Cu(4)	71.45 (9)
Cu(1)–S(14)–Cu(4)	97.9 (1)	Cu(2)–S(23)–Cu(3)	107.4 (1)
Cu(1)–S(12)–Cu(2)	127.9 (1)	Cu(3)–S(34)–Cu(4)	103.2 (1)
C(1)–S(1)–Cu(2)^{i}	95.8 (3)	C(2)–S(2)–Cu(1)^{ii}	95.0 (3)
Cu(1)–N(1)–C(1)	159.7 (8)	Cu(3)–N(3)–C(3)	170.9 (9)
N(1)–C(1)–S(1)	180 (2)	N(3)–C(3)–S(3)	178 (1)
Cu(2)–N(2)–C(2)	160.6 (8)	Cu()–N(4)–C(4)	168 (1)
N(2)–C(2)–S(2)	178 (1)	N(4)–C(4)–S(4)	178 (1)

[a] Symmetry operations: (i) $^1/_2 - x, -^1/_2 + y, ^3/_2 - z$; (ii) $^1/_2 - x, ^1/_2 + y, ^3/_2 - z$; (iii) $1 - x, 1 - y, 1 - z$.

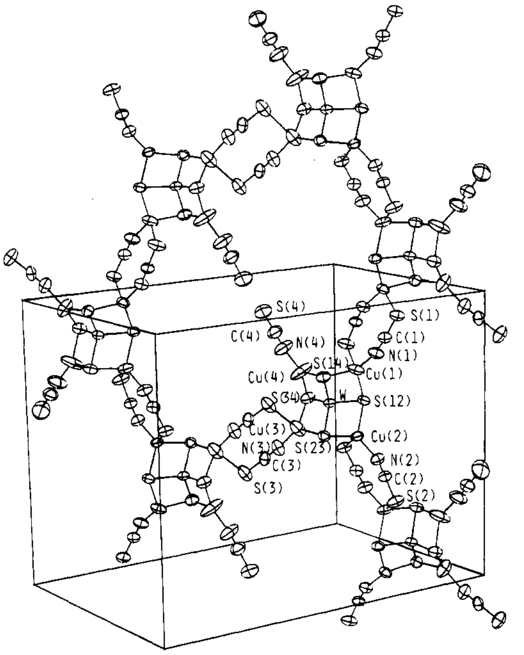

Figure 2. Perspective view (50% ellipsoids) of the polymeric $[(CuNCS)_4WS_4]^{2-}$ dianion showing the helical-chain structure. Atom labeling is indicated about the crystallographically independent unit. The origin of the unit cell lies at the bottom upper corner with *a* pointing from right to left, *b* going downward, and *c* going toward the reader.

Table V. Electronic Absorption Spectra of $[(CuNCS)_nMS_4]^{2-}$ Compounds in DMF Solutions

compds	λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[a]
$(PPh_4)_2WS_4$	400 (18.00), 280 (27.00)
$(PPh_4)_2[(CuNCS)_2WS_4]$	416 (6.88), 310 (sh), 298 (18.88)
$(PPh_4)_2[(CuNCS)_4WS_4]$	430 (4.4), 320 (sh)
$(NMe_4)_2[(CuNCS)_4WS_4]$[b]	430 (4.48), 320 (sh)
$(PPh_4)_2MoS_4$	476 (13.2), 322 (21.00)
$(PPh_4)_2[(CuNCS)_2MoS_4]$	494 (4.04), 344 (sh), 316 (15.04)
$(PPh_4)_2[(CuNCS)_4MoS_4]$	504 (2.4), 360 (sh)

[a] Abbreviation: sh, shoulder. [b] Reference 6.

per–sulfur distance (Cu(3)···S(3) = 3.042 (4) Å) between Cu(3) and a sulfur atom of a NCS group belonging to a different chain. As a direct manifestation of the weak interaction between Cu(3) and S(3) the sum of the angles about Cu(3) diminishes and Cu(3) adopts an environment between trigonal planar and pseudotetrahedral. These weak interactions between adjacent chains via the pseudobridging thiocyanate group N(3)–C(3)–S(3) lead to a two-dimensional-network polymer.

In the infinite sheets the $[(CuNCS)_4WS_4]^{2-}$ dianions are alternatingly above and below the diagonal (101) planes with the W atoms lying out of this mean plane by almost 0.08 Å. The space between the anionic two-dimensional networks is filled with the PPh_4 cations with no unusually short van der Waals contacts. There are no channels in this structure. The structure of **3** contrasts markedly with the structure of the analogous complex $(NMe_4)_2[(CuNCS)_4WS_4]$,[6] in which a three-dimensional polymeric array is observed comprising solely four-coordinated copper atoms with no particular directionality or layering. As commonly found in metal thiocyanato complexes, both bridging and terminal NCS groups are nearly linear with normal dimensions. The Cu–S–C angles are bent and are close to 100°, and the Cu–N–C angles lie between 160 and 180°.

Electronic Spectra. The electronic spectra for $[(CuNCS)_nMS_4]^{2-}$ dianions are given in Table V. The principal features are attributed to the charge-transfer transitions of the MS_4^{2-} moiety.[1,9,10] The longest wavelength absorptions are red-shifted as additional CuNCS units are bound to the central MS_4 core. The $(PPh_4)_2[(CuNCS)_2MS_4]$ complexes exhibit bands in the high-energy absorption range at 292 and 310 (sh) nm for

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(9) Clark, R. J. H.; Dines, T. J.; Wolf, M. L. *J. Chem. Soc., Faraday Trans. 2*, **1982**, *78*, 679.

(10) Clark, R. J. H.; Dines, T. J.; Proud, G. P. *J. Chem. Soc., Dalton Trans.* **1983**, 2019.

Table VI. Infrared Vibrational Absorptions (cm^{-1}) for the $[(CuNCS)_nMS_4]^{2-}$ Complexes[a]

compds	C–N str		C–S str		N–C–S bend and M–S str	
$(PPh_4)_2[(CuNCS)_2WS_4]$	2100 (sh)	2088 s	830 m		473 sh	455 s
$(PPh_4)_2[(CuNCS)_2MoS_4]$	2100 (sh)	2087 s	831 m		467 s	
$(PPh_4)_2[(CuNCS)_4WS_4]$	2109 s	2090 s	826 vw	796 w	462 m	443 s
$(PPh_4)_2[(CuNCS)_4MoS_4]$	2108 s	2090 s	830 vw	799 w		454 s
$(NMe_4)_2[(CuNCS)_4WS_4]$[b]	2122 s	2087 s		794 w, 776 w, 764 w, 747 w	470 w	440 s
$(NMe_4)_2[(CuNCS)_4MoS_4]$[b]	2122 s	2087 s		796 w, 776 w, 767 w, 747 w	469 w	450 s

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; vw, very weak. [b] Reference 6.

W and 316 and 344 (sh) nm for Mo. The spectra of $(PPh_4)_2[(CuNCS)_4MS_4]$ exhibit only a shoulder in those ranges. The electronic spectrum of $(NMe_4)_2[(CuNCS)_4WS_4]$ is similar in profile, wavelength, and intensity of the absorption bands to those of the corresponding $(PPh_4)_2[(CuNCS)_4WS_4]$. Hence, there is convincing spectroscopic evidence that the two different polymeric structures cleave in DMF solution to give the same absorbing species.

Infrared Spectra. There have been several vibrational spectroscopic studies on complexes involving the MS_4Cu_n core (n = 1–4) that provide significant data to assign the IR frequencies of complexes containing this moiety. For these compounds bands attributed to M–S (M = Mo, W) stretching vibrations[11] have been found in the region 422–516 cm^{-1}. The IR spectra of thiocyanate and related complexes have also been extensively studied because of the valuable tool of this technique in distinguishing the bonding mode of coordinated thiocyanate.[12,13]

The NCS deformation mode can be used to characterize the bond type, being a single band at 450–490 cm^{-1} for M-NCS and a band at 440–400 cm^{-1} for M-SCN. Consequently, the assignments of the bands attributed to δ(NCS) and ν(MS) falling in the same region preclude any reasonable assignment. The IR spectra for the studied complexes are compared in Table VI. This table includes also spectral data for $(NMe_4)_2[(CuNCS)_4MS_4]$. As pointed out in the literature,[12,13] the ν(CN) stretching frequency is generally observed in the range 2100–2050 cm^{-1} for N-bonded thiocyanate, 2130–2085 cm^{-1} for S-bonded NCS, and 2165–2065 cm^{-1} for bridging NCS groups. Bands attributable to the C–N stretching mode are observed at 2100 (sh) and 2088 cm^{-1} for **1** and **2** as required by metal–nitrogen bonding (isothiocyanato complex). In contrast for **3** and **4** these bands are located at 2109 and 2090 cm^{-1}, consistent with the metal–nitrogen and metal–sulfur bonding found for thiocyanate-bridged polymers. These conclusions are confirmed in the IR spectra of the thiocyanate-bridged polymers $(NMe_4)_2[(CuNCS)_4MS_4]$, where the C–N stretches are found at 2122 and 2087 cm^{-1}. The two-dimensional polymers present in the solid state for **3** and **4** do not persist in DMF solution as evidenced by the observation of only one sharp band at 2090 cm^{-1} characteristic of monomeric structures with N-bonded thiocyanate. This conclusion is also supported by our electronic spectroscopic experiments as mentioned above. The C–S frequency of NCS-containing compounds lies in the 690–850-cm^{-1} region. The position of the C–S band is a reliable feature for N- or S-bonding. It is currently admitted that absorptions near 700 cm^{-1} are related to S-bonding and near or above 800 cm^{-1} to N-bonding. Compounds **1** and **2** (N-bonded) display a band at 830 cm^{-1} attributed to the expected C–S stretching vibration. Compounds **3** and **4**, which are N-bonded and also both N- and S-bonded via NCS bridges, exhibit bands around 830 (N-bonding) and 800 cm^{-1}; the intense bands of the PPh_4 cation in the strategic region 750–650 cm^{-1} prevent any observation of the M–NCS–M configuration. The ν(CS) diagnosis is easier for $(NMe_4)_2[(CuNCS)_4MS_4]$, as observed in Table VI. In the far-infrared region weak absorption bands are observed, tentatively assigned to the Cu–NCS stretching.

Registry No. **1**, 111349-48-5; **2**, 111349-50-9; **3**, 111349-54-3; **4**, 111349-52-1.

Supplementary Material Available: Tables SI and SII, listing thermal parameters for non-hydrogen atoms, the derived hydrogen positions, distances and angles in the cation, and distances of copper atoms from bounding planes of the coordination polyhedrons for **1** and **3**, respectively (8 pages); tables of calculated and observed structure factors for **1** and **3** (49 pages). Ordering information is given on any current masthead page.

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(11) Clark, R. J. H.; Joss, S.; Zvagulis, M.; Garner, C. D.; Nicholson, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 1595 and references therein.

(12) Clark, R. J. H.; Williams, C. S. *Spectrochim. Acta* **1966**, *22*, 1081.

(13) Bailey, R. A.; Kozak, S. L.; Nicholson, T. W.; Milles, W. N. *Coord. Chem. Rev.* **1971**, *6*, 407.