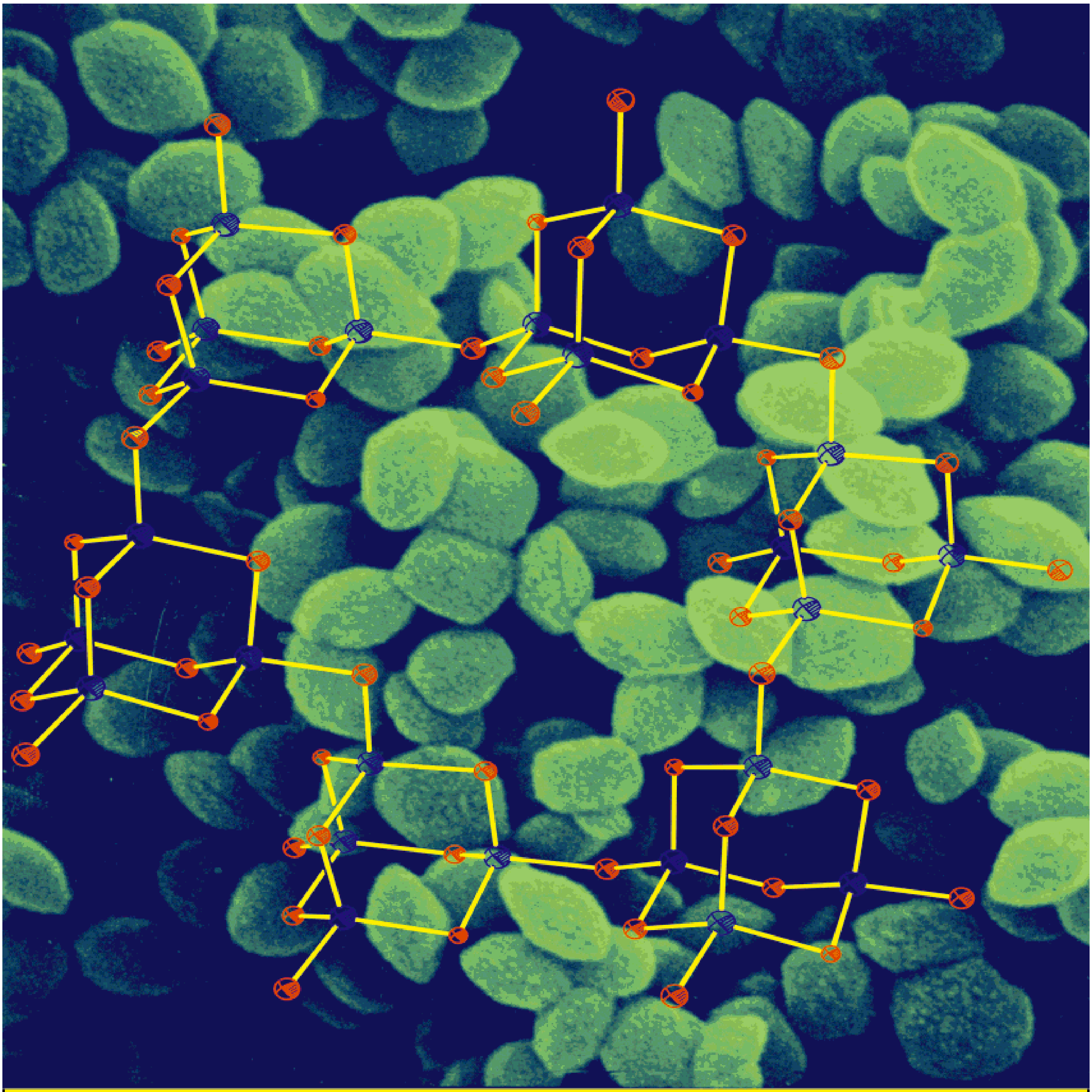


The high-temperature high-pressure phase of GeS_2 (δ) has been formed under very mild conditions by a rational assembly of adamantanoid $[Ge_4S_{10}]^{4-}$ clusters. An X-ray structure determination revealed two interpenetrating expanded cristobalite networks. Find out more on the following pages.

1433-7851/98/3715-2075 $ 17.50+.50/0

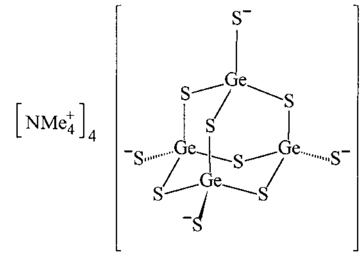
Synthesis and Crystal Structure of δ-GeS_2, the First Germanium Sulfide with an Expanded Framework Structure[**]

Mark J. MacLachlan, Srebri Petrov, Robert L. Bedard, Ian Manners,* and Geoffrey A. Ozin*

Germanium sulfides are attractive materials because of their interesting electronic and optical properties.[1] They have potential applications in hologram recording media, optical coatings, fiber optics, solid-electrolyte lithium batteries, and semiconductors.[1–4] Although one might expect germanium sulfides to adopt the myriad of topologies found in silicates and aluminosilicates (for example, zeolites), only dense phases of GeS_2 are known to date, and they are generally prepared under extreme conditions. Here we report the low-temperature self-assembly of adamantanoid $[Ge_4S_{10}]^{4-}$ clusters to form a crystalline modification of GeS_2 with an expanded framework.

The two common dense phases of GeS_2 are the α modification, a layered semiconductor that crystallizes in the monoclinic space group Pc, and the β modification, which crystallizes in the monoclinic space group $P2_1/c$.[5] Prewitt and Young reported a dense high-temperature and high-pressure γ-GeS_2 structure in which GeS_4 units are connected in a three-dimensional tetragonal cristobalite-related network (space group $I\bar{4}2d$).[6] Moreover, Viaene and Moh reported a high-pressure/high-temperature (γ) form of GeS_2 that is stable above 3000 bar at 600 °C and can be quenched to give a metastable phase at room temperature.[7] This phase was subsequently obtained by Wang and Horn from α-GeS_2 by hydrothermal synthesis at 1000 bar and 840 °C for 2 d, then 5000 bar at 575 °C for 7 d.[8] From powder diffraction data (ICCD PDF-2 Database, file no. 27-0239), they identified the crystalline phase as a tetragonal compound in the space group $I4_1/acd$ with $Z = 32$, but were unable to deduce its structure. Since 1973 this phase of GeS_2 has been absent from the literature. Although structures of other modifications were reported, no further studies of γ-GeS_2 were undertaken. In discussions of GeS_2, this form was frequently omitted or assumed to be identical to the phase described by Young et al. To avoid confusion with the γ-GeS_2 of Young et al., we renamed the phase described by Wang et al. as δ-GeS_2.

We have now discovered a low-temperature route to δ-GeS_2 which involves the polycondensation of $[(CH_3)_4N]_4Ge_4S_{10}$ (**1**) under acidic conditions. A representative scanning electron micrograph of crystals synthesized at 50 °C is shown in Figure 1. The material consists of fairly monodisperse rounded prisms. Energy dispersive X-ray analysis of the material established the composition to be GeS_2. Comparison of the Raman spectrum with that of the precursor **1** confirmed the presence of the adamantanoid cluster in the product (Figure 2). Notably, the spectra are similar in the skeletal



1

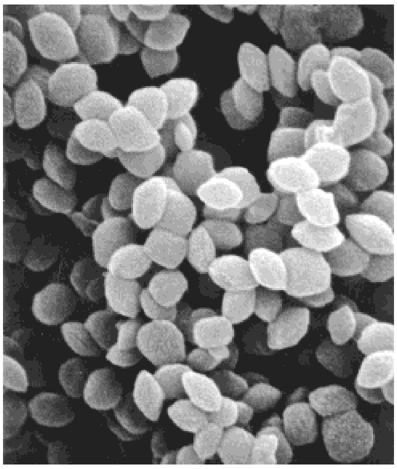


Figure 1. A scanning electron micrograph of crystalline δ-GeS_2 shows its fairly monodisperse rounded prism morphology. Average particle size approximately 200 nm.

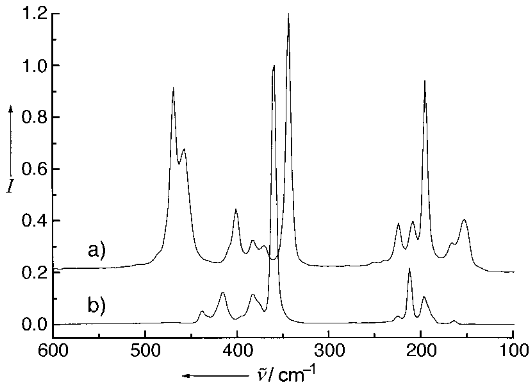


Figure 2. The Raman spectra of **1** (a) and crystalline δ-GeS_2 (b) are remarkably similar in the Ge–S stretching region. This confirms the presence of $[Ge_4S_{10}]$ clusters in the structure.

---

[*] Prof. Dr. I. Manners, Prof. Dr. G. A. Ozin, M. J. MacLachlan,
Dr. S. Petrov
Lash Miller Chemical Laboratories
University of Toronto
80 St. George Street, Toronto, M5S 3H6 (Canada)
Fax: (+1) 416-971-2011
E-mail: imanners@alchemy.chem.utoronto.ca
gozin@alchemy.chem.utoronto.ca
Dr. R. L. Bedard
UOP Research Center, Des Plaines, IL 60017-5017 (USA)

[**] Generous financial support of this work by the Natural Sciences and Engineering Research Council of Canada (NSERC) is deeply appreciated. Continuing support of the microporous metal chalcogenide work by UOP is gratefully acknowledged. G.A.O. acknowledges the Killam Foundation for the award of an Isaac Walton Killam Research Fellowship (1995–1997). I.M. and M.J.M. are indebted to NSERC for a Steacie Fellowship (1997–1999) and a post-graduate scholarship (1995–1999), respectively. We thank Dr. Neil Coombs for assistance with the recording of the SEM image.

region (470 – 140 cm^{-1}), and the most intense fully symmetrical Ge–S_t and Ge–S_b stretching frequencies (S_t and S_b = terminal and bridging S atoms) of the product are blue-shifted with respect to the precursor by about 20 cm^{-1}. This implies that the clusters are intact and interlinked in the product. Extremely weak Raman bands in the regions of C–H and S–H stretches indicate the presence of traces of surface-bound organic groups and thiol groups.

A detailed analysis of 47 unique reflections of the powder X-ray diffraction (PXRD) data confirmed the tetragonal space group $I4_1/acd$ (no. 142). Moreover, besides the necessary extinction conditions for this space group, additional special conditions were revealed: hkl: l, $h+k=2n+1$ and hkl: $l=2n$, $2k+l=4n$. These suggest the presence of atoms in special positions with the Wyckoff notations e (x, 0, 1/4) and d (0, 1/4, z). On the assumption that tetrahedral GeS_4 units would be the primary building blocks, as in all other GeS_2 structures, we concluded that the Ge atom and one S atom occupy general positions, and two S atoms special positions.

A suitable starting model for Rietveld refinement of δ-GeS_2 was an extremely hygroscopic polymorph of ZnI_2, which has a similar space group to δ-GeS_2.[9, 10] The result of the high-quality Rietveld refinement ($R_p = 8.4\,\%$) of δ-GeS_2 is shown in Figure 3. Atomic coordinates and isotropic displacement factors are presented in Table 1. Views of the adamantanoid [Ge_4S_{10}] cluster in the structure and the 24-atom ring composed of six Ge(μ-S)Ge-linked $Ge_4S_6S_{4/2}$ clusters in the network are shown in Figures 4a and 4b, respectively. The Ge–S bond lengths in the structure (2.194(4) – 2.225(4) Å) are nearly identical and, like the bond angles, are consistent with those observed in the other Ge_4S_{10}-based structures.[11–15]

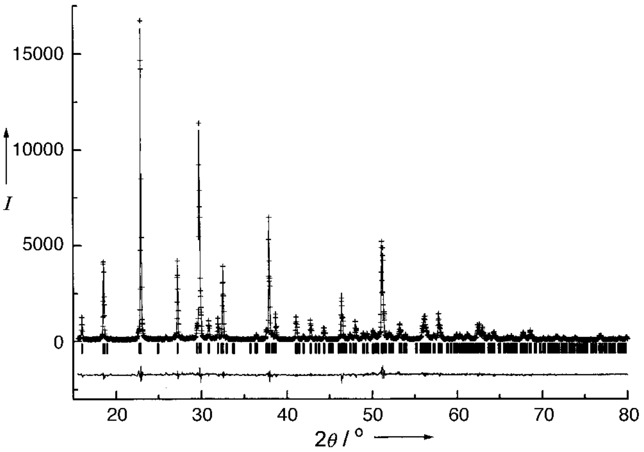


Figure 3. Observed (+), calculated (solid line), and difference (lower solid line) profiles from Rietveld refinement of the PXRD data of δ-GeS_2. I = intensity in arbitrary units.

Table 1. Atomic coordinates and isotropic displacement factors U_{iso} [$Å^2$] for δ-GeS_2

Atom	x/a	y/b	z/c	$U_{iso} \times 10^2$
Ge	0.3745(1)	0.3439(2)	0.0604(1)	2.77
S(1)	0.0	0.25	0.0124(2)	1.23
S(2)	0.2876(5)	0.0	0.25	2.18
S(3)	0.0345(3)	1.0166(3)	0.3760(2)	1.84

There is an intriguing topological relationship between the γ-GeS_2 structure of Young et al. and that of the new phase δ-GeS_2. Both are based on tetrahedral building blocks: GeS_4 in the former and Ge_4S_{10} in the latter. This can best be visualized by focusing on the Ge atoms and omitting the S atoms for the sake of clarity. Replacing the Ge atom in γ-GeS_2 by an adamantanoid Ge_4 cluster and applying the acentric space group of γ-GeS_2 ($I\bar{4}2d$) produces one of the interpenetrating frameworks of δ-GeS_2 (Figure 4c, d). The second interpenetrating framework of the δ form is the enantiomer of the first, to which it is related by a center of symmetry (Figure 4e, f), as indicated by the centric space group of the δ-form ($I4_1/acd$). In essence, the new structure is an expanded version of the earlier cristobalite-like structure of γ-GeS_2. An interesting analogy exists between the pairs γ-GeS_2/δ-GeS_2 and cristobalite/silica faujasite, in which tetrahedral SiO_4 units are replaced by $Si_{24}O_{48}$ sodalite cages to give the zeolite structure.[16] The expansion from Ge to Ge_4 structural units generates sufficient empty space for the co-crystallization of a second framework, which is the mirror image of the first.

We propose that the formation of δ-GeS_2 in the aqueous acidic medium occurs by a bimolecular nucleophilic substitution ("S_N2") reaction in which protonated $[Ge_4S_{10}]^{4-}$ clusters undergo condensation polymerization [(Eq. (1)].

$$\equiv Ge{-}SH + \equiv Ge{-}SH \rightarrow Ge{-}S{-}Ge\equiv + H_2S \qquad (1)$$

This leads to formation of the unexpected crystalline product δ-GeS_2 from the organized assembly of $[Ge_4S_{10}]^{4-}$ clusters [Eq. (2)], rather than the amorphous cross-linked network that would be expected from random polymerization of the clusters.

$$[(CH_3)_4N]_4Ge_4S_{10} + 4\,HCl \rightarrow 4\,GeS_2 + 4\,[(CH_3)_4N]Cl + 2\,H_2S \qquad (2)$$

In situ high-temperature powder X-ray diffraction indicates that the δ-GeS_2 phase is still stable above 620 °C. The volume of the unit cell increases steadily up to this temperature, while the c axis of the unit cell contracts slightly. Differential expansion/contraction effects of this type are well documented in uniaxial crystal systems whose lattices are composed of four-connected three-dimensional networks.[17] The phenomenon originates from thermally induced changes in bond angles between tetrahedral building blocks, which result in an untwisting of the entire network.

We have demonstrated, for the first time, the preparation of the high-pressure/high-temperature phase δ-GeS_2 in aqueous solution. This mild sol – gel process provides a novel route to a new type of IV/VI binary metal dichalcogenide whose structure is based upon two interpenetrating expanded cristobalite frameworks. The structure may serve as a model for other expanded XY_2 phases. With a suitable template or solvent, we believe the interpenetration of the networks can be eliminated to generate a new family of crystalline open-framework germanium sulfides with wide range of potential applications in the materials sciences.

Experimental Section

$[(CH_3)_4N)]_4Ge_4S_{10}$ (**1**) was prepared by a literature procedure.[12] δ-GeS_2 was prepared by two methods: a) Hydrochloric acid (9.6 mL, 0.22 M,

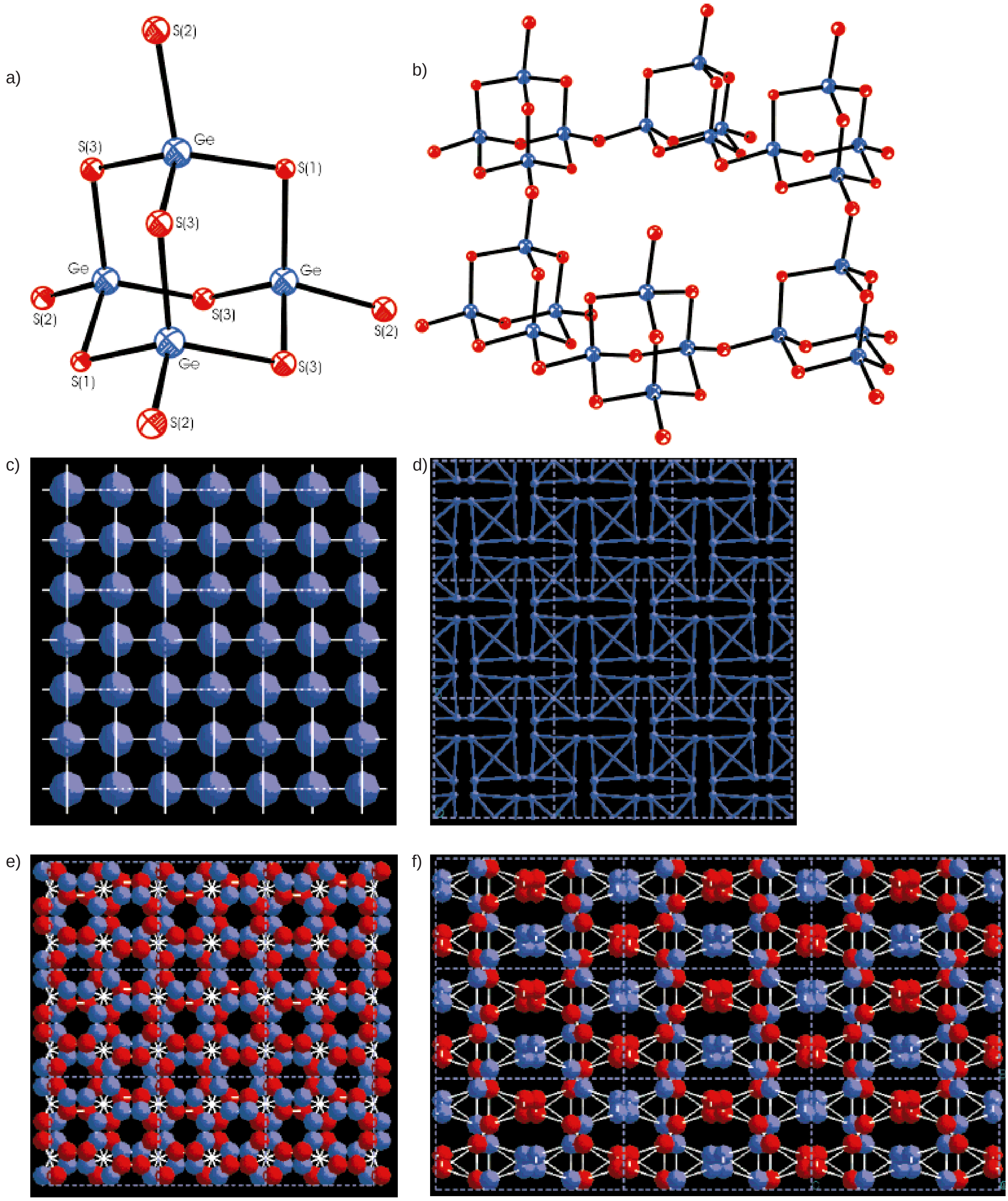


Figure 4. a) The adamantanoid [Ge_4S_{10}] cluster secondary building block of δ-GeS_2. b) The largest ring in each interpenetrating network of the δ-GeS_2 structure is a 24-atom [$Ge_{12}S_{12}$] ring that consists of six Ge(μ-S)Ge-linked [$Ge_4S_6S_{4/2}$] clusters. c) Projection of the structure of γ-GeS_2 reported by Young and Prewitt on the *ab* plane. d) Projection of the structure of one of the interpenetrating cristobalite-like networks in δ-GeS_2 on the *ab* plane. e) Projection of the two interpenetrating cristobalite-like networks in δ-GeS_2 on the *ab* plane. They are related by a center of symmetry to give interpenetrating enantiomeric frameworks. f) As in e), but with projection on the *ac* plane. (The S atoms are omitted from c)–f) for clarity.)

2.1 mmol) was added dropwise to a stirred solution of **1** (343 mg, 0.38 mmol) in 8.0 mL of water. The solution became viscous and cloudy, and H_2S was evolved. After 24 h at 50 °C, the off-white precipitate was isolated by centrifugation and washed with water, THF, and acetone to obtain 44 mg (22 %) of product. b) In a Teflon-lined vessel, **1** (579 mg, 0.638 mmol) in H_2O (1 mL) and hydrochloric acid (10 mL, 0.25 M, 2.5 mmol) were combined. A cloudy white mixture resulted. The vessel was sealed in a stainless-steel hydrothermal autoclave and heated to 150 °C for 24 h. Once cooled to room temperature, the off-white precipitate was isolated on a Buchner funnel and washed with water, THF, and acetone to give 157 mg (44 %) of δ-GeS_2. PXRD confirmed the crystallinity of both δ-GeS_2 products.

The PXRD analysis of δ-GeS_2 was carried out on a Siemens D5000 diffractometer with Bragg–Brentano $\theta/2\theta$ geometry. The source radiation ($Cu_{K\alpha}$, $\lambda = 1.54059$ Å) was obtained from a high-power line-focus Cu target, and the secondary beam was monochromatized by a Kevex solid-state detector. The diffraction pattern was initially indexed with the program ITO,[18] which provided a tetragonal, I-type unit cell. Further lattice refinement was performed with the Appleman and Evans program[19] by using the first 51 measured reflections (34 unique) within the range $14 \leq 2\theta \leq 70°$. The refinement [$M_{20} = 23.3$, $F_{30} = 27.5$ (0.012, 89)] gave the space group $I4_1/acd$ (no. 142) based on both general and special conditions for systematic absences/extinctions, as discussed in the text. Several other related space groups were also tested as possible sub- or superlattices, but were not fitted successfully. The final structure was obtained by refinement of atomic parameters with the program GSAS 6.0 (PC version).[20] Crystallographic data for δ-GeS_2: $I4_1/acd$, $a = 11.0650(1)$, $c = 18.7178(2)$ Å, $V = 2291.71$ Å^3, $\rho_{calcd} = 3.17$ g cm^{-3}, $Z = 32$, $R_{wp} = 0.1159$, $R_p = 0.0842$, $R_{Bragg} = 0.0927$, $\chi^2 = 4.351$, measurement range $12 \leq 2\theta \leq 80°$, 3400 data points, 372 observed reflections, 34 parameters refined. The peak profiles were fitted by a pseudo-Voigt function,[21] and a Finger–Cox–Jephcoat asymmetry correction was applied.[22]

Raman spectra were recorded on a Bomems MB-157 FT spectrometer with an InGaAs NIR laser (100 mW). The instrument was configured in the 180° backscattering mode, and samples were sealed in glass capillary tubes. Spectra were recorded with a resolution of 4 cm^{-1}, and about 100 scans were made to achieve an excellent signal-to-noise ratio.

Received: January 22, 1998 [Z 11391 IE]
German version: *Angew. Chem.* **1998**, *110*, 2185–2189

Keywords: clusters · germanium · solid-state structures · sulfur · sol–gel processes

[1] a) M. Saji, H. Kubo, *Nagoya Kogyo Daigaku Gakuho* **1981**, *32*, 213; b) Z. G. Ivanova, *Thin Solid Films* **1995**, *256*, 257; c) A. A. Lavrentyev, A. N. Gusatinskii, I. Y. Nikiforov, N. Y. Safontseva, *Physica B* **1995**, *209*, 344; d) D. R. Simons, A. J. Faber, H. Dewaal, *J. Non-Cryst. Solids* **1995**, *185*, 283; e) D. Marchese, G. Kakarantzas, A. Jha, B. N. Samson, J. Wang, *J. Mod. Optics* **1996**, *43*, 963.

[2] P. P. Pogoretskii, E. N. Sal'kova, M. S. Soskin, D. I. Bletskan, I. F. Kopinets (Institute of Physics, Academy of Sciences, Ukranian S.S.R.), SU-B 453976, **1976** [*Chem. Abstr.* **1976**, *85*, 134491z].

[3] M. Haase, H. Bechtel, W. Czarnojan, D. Waedow (Philips Electronics N.V.), EP-B 714966, **1996** [*Chem. Abstr.* **1996**, *125*, 99556v].

[4] S. Kondo, K. Takada (Matsushita Electric Ind. Co. Ltd.), JP-B 05205741, **1993** [*Chem. Abstr.* **1994**, *120*, 34524k].

[5] a) G. Dittmar, H. Schäfer, *Acta Crystallogr. B* **1976**, *32*, 1188; b) G. Dittmar, H. Schäfer, *Acta Crystallogr. B* **1975**, *31*, 2060; c) D. I. Bletskan, I. M. Mitrovtsii, V. A. Stefanovich, M. V. Potorii, Yu. V. Voroshilov, V. Yu. Slivka, *Sov. Phys. Crystallogr. (Engl. Transl.)* **1987**, *32*, 224.

[6] C. T. Prewitt, H. S. Young, *Science* **1965**, *149*, 535.

[7] W. Viaene, G. H. Moh, *Neues Jahrb. Mineral. Abh.* **1973**, *119*, 113.

[8] N. Wang, E. Horn, *Neues Jahrb. Mineral. Monatsh.* **1973**, 413.

[9] P. P. H. Fourcroy, D. Carré, J. Rivet, *Acta Crystallogr. B* **1978**, *34*, 3160.

[10] Other structures with similar frameworks are known. For example, an Na_2SnAs_2 Zintl phase which is isostructural and isoelectronic to δ-GeS_2 has been prepared from the elements: M. A. Asbrand, B. Eisenmann, *Z. Naturforsch. B* **1993**, *48*, 452.

[11] O. M. Yaghi, Z. Sun, D. A. Richardson, T. L. Groy, *J. Am. Chem. Soc.* **1994**, *116*, 807.

[12] C. L. Bowes, A. J. Lough, A. Malek, G. A. Ozin, S. Petrov, D. Young, *Chem. Ber.* **1995**, *129*, 283.

[13] C. L. Cahill, J. B. Parise, *Chem. Mater.* **1997**, *9*, 807.

[14] T. Kemin, A. Darovsky, J. B. Parise, *J. Am. Chem. Soc.* **1995**, *117*, 7039.

[15] K. Tan, Y. Ko, J. B. Parise, A. Darovsky, *Chem. Mater.* **1996**, *8*, 448.

[16] W. M. Meier, D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd ed., Butterworth-Heinemann, Toronto, **1992**.

[17] D. Taylor, *Br. Ceram. Trans. J.* **1992**, *9*, 217.

[18] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89.

[19] D. E. Appleman, H. T. Evans, Jr., Job 9214, *U.S. Geol. Survey* **1973** NTIS, Doc. PB2–16188; revised PC version by P. H. Benoit, **1987**.

[20] R. B. von Dreele, A. C. Larson, *General Structure Analysis System*, Los Alamos National Laboratory Report LAUR 86–748, **1990**.

[21] P. Thompson, D. E. Cox, J. B. Hastings, *J. Appl. Crystallogr.* **1987**, *20*, 79.

[22] L. W. Finger, D. E. Cox, A. P. Jephcoat, *J. Appl. Crystallogr.* **1994**, *27*, 892.

Metal–Metal "Communication" of Rh or Pd with Nd in Novel Heterobinuclear Complexes**

Anke Spannenberg, Markus Oberthür, Henrik Noss, Annegret Tillack, Perdita Arndt, and Rhett Kempe*

Dedicated to Professor Carl Krüger
on the occasion of his 65th birthday

For heterobinuclear complexes which contain an early and a late transition metal and in which the metal centers can "communicate" with one another, interesting properties have been predicted, such as multifunctionality and cooperative effects.[1] However, the problems encountered in the realization of the differing coordination chemical requirements of both metals in close proximity to one another are just as great as the expectations.[2] We report here on the synthesis and structure of heterobinuclear complexes in which interactions of Group 9 (Rh) or Group 10 (Pd) metals with a lanthanide (Nd) are possible.[3] A decisive factor for this enlargement of the class of "early–late heterobimetallics" (ELHB) is a novel ligand system incorporating bisaminopyridinato ligands.[4]

If two equivalents of dilithiated $O(SiMe_2ApH)_2$ are treated in situ with $NdCl_3$ in THF, the neodymium "ate" complex **1** is obtained in good yields as a violet, crystalline compound (Scheme 1; $O(SiMe_2ApH)_2 = O[Si(CH_3)_2NH\text{-}(4\text{-}CH_3C_5H_3N)]_2$). The IR spectrum of **1** displays the signals typical for $O(SiMe_2Ap)_2$, and the elemental analysis is in agreement with the formula given in Scheme 1. The reaction of **1** with $[\{(cod)RhCl\}_2]$ (cod = 1,5-cyclooctadiene) in *n*-hexane gives yellow crystals of the heterobinuclear compound **2** (Scheme 1). The X-ray crystal structure analysis[5] of this compound (Figure 1) shows there is an almost square-planar coordination geometry at the rhodium center,[6] and that two amido N atoms coordinate the {Rh(cod)} fragment (N(1)-Rh(1)-N(3) 84.1(5)°). For the aminopyridinato fragments,

---

[*] Dr. R. Kempe, Dr. A. Spannenberg, Dr. M. Oberthür, Dipl.-Chem. H. Noss, Dr. A. Tillack, Dr. P. Arndt
Abt. Komplexkatalyse
Institut für Organische Katalyseforschung an der Universität
Buchbinderstrasse 5–6, D-18055 Rostock (Germany)
Fax: (+49) 381-466-9374
E-mail: rkempe@chemie1.uni-rostock.de

[**] This work was supported by the Max-Planck-Gesellschaft and by the Fonds der Chemischen Industrie. We are grateful to Prof. Rosenthal for his support of our work.