five-coordinated with the N atoms of tren located at four corners of a trigonal bipyramid. The crystal structure of [Co(tren) (NCS)$_2$]NCS.H$_2$O was investigated in order to decide whether the N or the S atoms of the thiocyanate groups were attached to the Co atom and whether there were differences in bond lengths between free and coordinated thiocyanate groups.

The [Co(tren) (NCS)$_2$]$^+$ ion has the *cis*-octahedral configuration with six N atoms coordinated to Co. The thiocyanate ion is known to be coordinated to trivalent Co through the N atom in [Coen$_2$SO$_3$NCS]. 2H$_2$O (Baggio & Becka, 1969). [Co(SCN) (NH$_3$)$_5$]Cl$_2$ is known to exist in two isomeric forms, one in which the S atom is coordinated to Co and another which is an isothiocyanate isomer (Snow & Boomsma, 1972). There are no significant differences in bond lengths between the free thiocyanate group and the coordinated ones. The bond lengths found are in close agreement with those reported in other structures. The tren molecule exhibits rather large differences in bond lengths from corresponding lengths reported for tren(HCl)$_3$. Because of the high absorption, the bond lengths between light atoms may be subject to large errors and the significance of the differences may be doubtful. The Co–N distances are on average 0·1 Å lower than the corresponding Me–N distances in the Ni^{II}, Cu^{II} and Zn^{II}-tren complexes.

The structure is held together by ionic forces and by weak hydrogen bonds from amino N atoms to water [N (3)–O 2·945 Å], to the free thiocyanate ion [N (1)–S (2) 3·447, N (3)–S (2) 3·372, N (1)–N (7) 3·084, N (5)–N (7) 2·897 Å] and to an S atom of a neighbouring molecule [N (5)–S (1) 3·356 Å].

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References

Baggio, S. & Becka, L. N. (1969). *Acta Cryst.* **B25**, 946–954.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

Grønbæk Hazell, R. & Rasmussen, S. E. (1968). *Acta Chem. Scand.* **22**, 348–350.

Hazell, A. C. (1967). *Acta Cryst.* **23**, 1096.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jain, P. C. & Lingafelter, E. C. (1967). *J. Amer. Chem. Soc.* **89**, 6131–6136.

Johnson, C. K. (1965) *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Pepinsky, R. & Okaya, Y. (1956). *Phys. Rev.* **103**, 1645–1647.

Rasmussen, S. E. (1959). *Acta Chem. Scand.* **13**, 2009–2022.

Rasmussen, S. E. & Grønbæk Hazell, R. (1963). *Acta Chem. Scand.* **17**, 832–842.

Snow, M. R. & Boomsma, R. F. (1972). *Acta Cryst.* **B28**, 1908–1913.

Stewart, J. M. (1963). X-RAY 63, Univ. of Maryland, U.S.A.

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Refinement of the Crystal Structure of Nb$_5$Ge$_3$

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Abstract. Nb$_5$Ge$_3$, $M=682{\cdot}3$, tetragonal, $I4/mcm$, $a=b=10{\cdot}146$ (7), $c=5{\cdot}136$ (4) Å, $U=530$ Å^3, $Z=4$, $D_c=8{\cdot}55$ g cm^{-3}. Mo $K\alpha$ radiation, $\mu=267{\cdot}5$ cm^{-1}. The structure has been refined to $R=0{\cdot}017$ from single-crystal diffractometer data (189 independent reflexions).

Introduction. A rod of nominal composition 3Nb + Ge was prepared by isostatic pressing of a mixture of Nb (Alpha, 99·8 %) and Ge powders (Koch–Light, 99·999 %). The rod was sintered in a helium atmosphere at about 1000 °C and zone-refined three times by the floating zone technique. Needle-shaped small crystals were observed in the last zone to solidify. The crystals proved to belong to the tetragonal Nb$_5$Ge$_3$ phase. An X-ray diffraction investigation was undertaken in order to check the composition and structure of the crystals. Powder photographs of filings from nearby areas of the rod showed that the phases Nb$_3$Ge and Nb$_5$Ge$_3$ were both present.

A crystal, $0{\cdot}002\times0{\cdot}002\times0{\cdot}025$ cm, was mounted along **c** and intensities were measured out to sin $\theta_{\max}=$

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Table 1. *Atomic coordinates, expressed as fractions of the cell edges, and thermal parameters* (Å$^2 \times 10^{-4}$)

Estimated standard deviations are given in parentheses. The anisotropic temperature coefficient is $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	4(*b*)	0·00000	0·50000	0·25000	49 (7)	49	60 (6)	0	0	0
Nb(2)	16(*k*)	0·07605 (7)	0·22220 (6)	0·00000	45 (3)	48 (4)	88 (4)	0 (2)	0	0
Ge(1)	4(*a*)	0·00000	0·00000	0·25000	53 (8)	53	72 (7)	0	0	0
Ge(2)	8(*h*)	0·16546 (17)	0·66546	0·00000	52 (7)	52	105 (6)	1 (4)	0	0

0·5 with a computer-steered Supper diffractometer (Kryger, 1975) with monochromatic Mo $K\alpha$ radiation. Correction was made for Lorentz and polarization effects (Kryger, 1975) and symmetry-related reflexions were averaged, 189 independent reflexions for which $F_o^2 > 3{\cdot}0\sigma(F_o^2)$, according to counting statistics, were used in the subsequent calculations. A correction was applied for absorption, the crystal being approximated to a cylinder of radius 0·001 cm.

A Patterson function confirmed the structure reported by Nowotny, Searcy & Orr (1956), with the exception that y for the Nb atom in 16(k) was approximately 0·22 instead of 0·27 [*cf. Structure Reports* (1956)]. Full-matrix least-squares refinement (*LINUS*: Busing, Martin & Levy, 1962; Coppens & Hamilton, 1970) of positional and anisotropic thermal parameters yielded $R=0{\cdot}017$ ($R_w=0{\cdot}021$) for 16 parameters. The quantity minimized was $\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2$ with $w=1$. The scattering factors were those of Cromer & Mann (1968) corrected for anomalous dispersion (Cromer & Liberman, 1970). R and R_w are $\sum||F_o|-|F_c||/\sum|F_o|$ and $[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, respectively. Atomic coordinates and thermal parameters are given in Table 1 and interatomic distances (*ORFFE*: Busing, Martin & Levy, 1964) less than 4·0 Å in Table 2.*

Table 2. *Interatomic distances* (Å) *less than* 4·0 Å

Estimated standard deviations are 0·002 Å.

Notation

Superscript		Superscript	
i	$-x,\ 1-y,\ 1-z$	vii	$-x,\ 1-y,\ -z$
ii	$\frac{1}{2}-y,\ \frac{1}{2}-x,\ z$	viii	$y-\frac{1}{2},\ \frac{1}{2}-x,\ \frac{1}{2}-z$
iii	$-x,\ y,\ \frac{1}{2}-z$	ix	$-x,\ -y,\ 1-z$
iv	$y,\ x,\ \frac{1}{2}+z$	x	$x,\ y-1,\ z$
v	$-y,\ x,\ z$	xi	$\frac{1}{2}-x,\ \frac{3}{2}-y,\ \frac{1}{2}-z$
vi	$1-y,\ x,\ z$		

		Number of bonds
Nb(1)–Ge(2)	2,699	4 [2Ge(2)–Nb(1) bonds]
Nb(1)–Nb(1$^{\rm i}$)	2·568	2
Nb(1)–Nb(2)	3·192	8
Ge(1)–Nb(2)	2·707	8
Ge(1)–Ge(1$^{\rm ix}$)	2,568	2
Nb(2)–Ge(1)	2·707	2
Nb(2)–Ge($^{\rm vi}$)	2·685	1 [2Ge(2)–Nb(2) bonds]
Nb(2)–Ge(2$^{\rm vii}$)	2·702	1 [2Ge(2)–Nb(2) bonds]
Nb(2)–Ge(2$^{\rm viii}$)	2·952	2 [4Ge(2)–Nb(2) bonds]
Nb(2)–Nb(2$^{\rm ii}$)	2·895	1
Nb(2)–Nb(2$^{\rm iii}$)	2·996	2
Nb(2)–Nb(1)	3·192	2
Nb(2)–Nb(2$^{\rm iv}$)	3·316	2
Nb(2)–Nb(2$^{\rm v}$)	3·370	2
Ge(1)–Ge(2$^{\rm xi}$)	3·533	
Ge(2)–Ge(2$^{\rm v}$)	3·998	

Discussion. The X-ray results indicate that the sample investigated has the stoichiometric composition Nb_5Ge_3 within the errors of measurement. As it was formed from a mixture of a different composition, we conclude that the composition range for Nb_5Ge_3 is narrow. Crystals of Nb_5Ge_3 have also been prepared by melting the two elements together in the stoichiometric proportions and in this case too several phases were observed.

The interatomic distances given in Table 2 differ significantly from most of those quoted in *Structure Reports* (1956) although the structure reported there is correct in principle. The unit cell contains one Nb atom, Nb(1), at a fourfold position, one Ge atom, Ge(1), likewise at a fourfold position, another Nb atom, Nb(2), at a 16-fold position and a Ge atom, Ge(2) at an eightfold position. Ge(1) is surrounded by eight Nb(2) atoms which form a square Archimedean antiprism with the Ge atom at the centre. The antiprisms share the square faces and form chains along **c**. The Ge atoms in the centres of the antiprisms are within bonding distance (2·568 Å) of each other. Ge(2) is bound to two Nb(1) and eight Nb(2) with distances ranging from 2·69 to 2·95 Å. Nb(1) has four Ge(2) neighbours tetrahedrally coordinated, two other Nb(1) neighbours at 2·57, and eight Nb(2) neighbours at 3·19 Å. The short Nb–Nb bond is along **c**. Nb(2) has 15 nearest neighbours as shown in Table 2. In Nb metal each Nb atom has eight nearest neighbours at 2·86 and six other neighbours at 3·30 Å. Table 2 shows that in Nb_5Ge_3 the Nb–Nb lengths along **c** are appreciably smaller than the shortest Nb–Nb bond in pure Nb and that most Nb–Nb distances are smaller than the distance between next nearest neighbours in pure Nb. Only one type of Ge–Ge bond occurs (2·568 Å). The Ge atoms are mainly bound to Nb atoms.

The short distances along **c** indicate that crystals of Nb_5Ge_3 should be anisotropic with respect to several physical properties. Attempts to grow larger crystals of this compound continue.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31304 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The crystals used in this investigation were prepared by Miss Britta Lundtoft.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

KRYGER, L. (1975). Thesis. Univ. of Aarhus, Denmark.

NOWOTNY, H., SEARCY, A. W. & ORR, J. E. (1956). *J. Phys. Chem.* **60**, 677–678.

Structure Reports (1956). **20**, 109–110.

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2-Amino-3-nitropyridine

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Abstract. $C_5H_5N_3O_2$, monoclinic, space group $P2_1/n$; $a=8{\cdot}743(1)$, $b=4{\cdot}898(1)$, $c=14{\cdot}473(1)$ Å, $\beta=106{\cdot}57$ (1)°, $V=594$ Å^3, $Z=4$, $D_m=1{\cdot}54$ (1), $D_c=1{\cdot}553$ g cm^{-3}, μ(Cu $K\alpha$) = 10·7 cm^{-1}. The molecule is closely planar, the nitro group being rotated by less than 3°. The structure features an off-set stacking of parallel pyridine rings at a separation of about 3·16 Å, and hydrogen bonding across centres of symmetry to form dimers.

Introduction. Crystals of 2-amino-3-nitropyridine are yellow needles elongated along **b**. Cell dimensions were obtained by a least-squares fit to the $\sin^2\theta$ values of 56 hkl reflexions measured on a diffractometer. No corrections for eccentricity or absorption were made, and weights were assumed as inversely proportional to $\sin^2 2\theta$. The space group $P2_1/n$ was indicated by the absences $h0l$ with $(h+l)$ odd and $0k0$ with k odd. The density was measured by flotation in dilute K_2HgI_4 solution.

A crystal, 0·30 × 0·20 × 0·15 mm, sealed in a Lindemann glass capillary, was mounted on a computer-controlled Syntex $P\bar{1}$ diffractometer. Intensities were collected with Cu $K\alpha$ radiation [λ(Cu $K\alpha$) = 1·5418 Å; graphite monochromator] and a variable rate θ–2θ scan technique. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. A single standard reflexion was checked after each 45 intensity measurements; it showed no significant drift in intensity. A correction for coincidence losses at high counting rates was applied according to $I_c=[1-(1-4\tau I_o)^{1/2}]/2\tau$, where I_c and I_o are the corrected and observed intensities, respectively, and τ is the dead time, for which a value of $2{\cdot}1\times10^{-6}$ was calculated from empirical data. The data set consisted of 985 observed reflexions (*i.e.*

Table 1. *Final atomic parameters and standard deviations* (*in parentheses*)

The anisotropic temperature coefficients are in the form $T_l=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$.

Fractional coordinates are × 10^5 for heavy atoms, × 10^3 for hydrogen atoms. Anisotropic temperature coefficients are × 10^4, isotropic B's × 10.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	40401 (23)	25785 (40)	56456 (13)	154 (3)	407 (10)	41 (1)	11 (5)	26 (1)	−1 (2)
C(2)	32173 (25)	16128 (49)	47594 (14)	128 (3)	355 (11)	40 (1)	55 (5)	25 (2)	8 (3)
C(3)	21437 (25)	−5798 (49)	46982 (14)	125 (3)	399 (12)	40 (1)	31 (5)	21 (2)	−3 (3)
C(4)	19416 (28)	−17417 (57)	55308 (17)	138 (4)	430 (13)	52 (1)	6 (6)	31 (2)	7 (4)
C(5)	27964 (30)	−7537 (58)	64098 (17)	177 (4)	524 (15)	43 (1)	7 (6)	36 (2)	18 (4)
C(6)	38186 (31)	13976 (59)	64219 (17)	172 (4)	493 (14)	41 (1)	−5 (7)	24 (2)	−6 (3)
N(2)	35207 (27)	29200 (50)	40207 (15)	181 (4)	471 (12)	41 (1)	−3 (6)	28 (2)	19 (3)
N(3)	12528 (24)	−17335 (46)	37890 (13)	152 (3)	491 (12)	47 (1)	21 (5)	18 (2)	−3 (3)
O(1)	14801 (23)	−8376 (45)	30413 (12)	268 (4)	682 (12)	40 (1)	−64 (6)	21 (1)	2 (3)
O(2)	2980 (21)	−35806 (44)	37814 (12)	180 (3)	651 (11)	71 (1)	−99 (5)	20 (2)	−25 (3)