Acta Cryst. (1975). B**31**, 2879

2,2′,2″-Triaminotriethylaminebisisothiocyanatocobalt(III) Thiocyanate Monohydrate

BY F. A. KUNDELL,* R. G. HAZELL† AND S. E. RASMUSSEN†

*Department of Inorganic Chemistry, Aarhus University, DK-*8000 *Aarhus C, Denmark*

(*Received* 17 *June* 1975; *accepted* 19 *June* 1975)

Abstract. $Co[N(CH_2.CH_2.NH_2)_3(NCS)_2](NCS).H_2O$, orthorhombic, *Iba*2, $Z=8$, F.W. 397·31, $a=15·615$, $b=16·22$, $c=13·63$ Å, $V=3452·1$ Å^3, $D_m=1·520$, $D_c=1·528$ g cm^{-3}, λ(Cu $K\beta$)$=1·3922$ Å. $R=6·0\%$. The cation has an octahedral configuration with the two isothiocyanate groups *cis*. The free thiocyanate ion and the two bound isothiocyanate groups show no significant differences in bond lengths.

Introduction. The compound was prepared from 2,2′,2″-triaminotriethylamine, $CoCl_2$, air, water and KNCS. Dark-red crystals were obtained: Co found 15·54%, calc. 15·52%. One crystal was ground to a cylinder of diameter 0·26, length 4 mm. Weissenberg and precession photographs showed that the crystals were orthorhombic with systematic absences $h+k+l\neq 2n$, $0kl$: $k\neq 2n$, $h0l$: $h\neq 2n$. The crystals were piezoelectric and hence the space group was assumed to be *Iba*2 (No. 45). The density, measured by flotation, was 1·520 g cm^{-3}. Intensities were measured with a Supper–Pace automatic equi-inclination Weissenberg-type diffractometer. Cu $K\beta$ radiation was selected by a LiF monochromator. Reflexions with $l=0$ to 14 were measured to a $\sin\theta/\lambda$ limit of 0·67 Å^{-1}. Reflexions with $l=0$ to -9 were obtained on an Arndt–Phillips linear diffractometer. Cu $K\beta$ radiation was selected by a graphite monochromator. The radius of the limiting half sphere was 0·34 Å^{-1} for the latter data.

The even Patterson function $P_c(u)$ was calculated with data with $l\geq 0$. The odd Patterson function $P_s(u)$ (Pepinsky & Okaya, 1956) was computed with all data within a limiting sphere of radius $\sin\theta/\lambda=0·34$ Å^{-1}. The resolution of the $P_s(u)$ function only allowed the positions of the Co and S atoms to be determined and these findings were corroborated by the even Patterson function. The full structure was determined from successive electron-density maps. Positional and vibrational parameters were refined by least-squares calculations. The parameters are given in Table 1.‡ Bond distances and angles are given in Table 2. The structure is depicted in Figs. 1 and 2. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962); the correction for anomalous

Table 1. *Fractional coordinates and temperature-factor parameters*

Standard deviations of the last digits are in parentheses.

(*a*) Non-hydrogen atoms. Values are $\times 10^4$. U_{ij} are in Å^2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2522 (1)	1776 (1)	0 (0)	271 (6)	410 (8)	306 (8)	−10 (8)	9 (7)	−11 (9)
S(1)	1141 (2)	1166 (2)	2976 (3)	423 (16)	508 (22)	399 (19)	−69 (15)	125 (17)	50 (18)
S(2)	3624 (2)	1193 (3)	2913 (4)	372 (16)	600 (26)	509 (22)	6 (16)	−153 (17)	−49 (23)
S(3)	4245 (3)	3828 (3)	1265 (4)	431 (18)	605 (25)	623 (24)	188 (18)	15 (18)	−213 (23)
N(1)	3506 (7)	1071 (8)	395 (11)	389 (57)	396 (65)	375 (73)	157 (49)	25 (55)	21 (58)
N(2)	3039 (8)	2745 (9)	555 (10)	494 (68)	497 (72)	420 (74)	59 (60)	128 (56)	−177 (60)
N(3)	1462 (8)	2332 (8)	−348 (11)	347 (57)	364 (68)	362 (59)	−54 (52)	0 (49)	139 (55)
N(4)	2056 (6)	821 (7)	−650 (9)	210 (46)	449 (64)	359 (64)	−9 (43)	−21 (41)	3 (50)
N(5)	3044 (7)	2046 (8)	−1207 (9)	350 (56)	396 (69)	427 (76)	−59 (49)	135 (51)	−213 (57)
N(6)	1986 (7)	1490 (9)	1233 (9)	340 (55)	673 (81)	230 (56)	−69 (53)	−16 (48)	39 (63)
N(7)	5281 (10)	1290 (11)	3626 (21)	419 (84)	751 (118)	1990 (246)	26 (75)	−633 (124)	−11 (142)
C(1)	2413 (10)	58 (10)	−140 (13)	451 (75)	417 (71)	595 (127)	−2 (70)	55 (71)	84 (73)
C(2)	3329 (9)	197 (9)	69 (17)	420 (66)	483 (89)	620 (96)	94 (58)	−191 (83)	153 (94)
C(3)	1087 (9)	908 (11)	−584 (15)	282 (69)	605 (106)	674 (120)	−73 (65)	62 (71)	−95 (86)
C(4)	1627 (9)	1365 (8)	1954 (11)	368 (66)	255 (67)	455 (90)	15 (48)	−81 (60)	12 (59)
C(5)	3549 (9)	3197 (10)	849 (11)	400 (67)	458 (79)	353 (69)	−8 (64)	6 (57)	−25 (69)
C(6)	843 (8)	1759 (9)	−824 (11)	253 (56)	464 (86)	517 (87)	122 (59)	−37 (54)	−135 (71)
C(7)	2347 (8)	822 (8)	−1712 (11)	371 (67)	336 (67)	367 (71)	5 (52)	100 (52)	−167 (55)
C(8)	2574 (9)	1645 (9)	−2030 (11)	426 (69)	587 (86)	332 (71)	−285 (67)	156 (64)	−26 (66)
C(9)	4591 (10)	1214 (11)	3351 (16)	433 (81)	472 (95)	797 (134)	−63 (68)	−110 (82)	134 (95)
O	366 (8)	2983 (10)	1242 (13)	616 (86)	1099 (128)	1253 (141)	231 (81)	467 (95)	−455 (112)

---

* Present address: Salisbury State College, Salisbury, Maryland 21801, U.S.A.

† Authors to whom correspondence should be addressed.

‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31214 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

(*b*) Hydrogen atoms. Values of fractional coordinates are $\times 10^3$.

H(11)	225 (13)	42 (12)	−60 (15)	4·8 (43)
H(12)	218 (9)	25 (8)	35 (12)	2·6 (30)
H(21)	378 (10)	17 (9)	−71 (12)	2·8 (35)
H(22)	358 (10)	−9 (12)	56 (14)	5·5 (41)
H(31)	96 (8)	64 (8)	−2 (11)	1·7 (25)
H(32)	83 (8)	53 (8)	−127 (10)	3·0 (27)
H(61)	34 (7)	195 (7)	−59 (9)	1·6 (21)
H(62)	83 (9)	178 (9)	−161 (11)	2·8 (33)
H(71)	198 (12)	49 (12)	−199 (16)	6·6 (47)
H(72)	284 (8)	50 (8)	−183 (11)	2·8 (28)
H(81)	212 (17)	197 (15)	−173 (22)	9·4 (71)
H(82)	280 (9)	180 (9)	−247 (11)	3·3 (28)
H(N11)	405 (14)	114 (12)	−21 (17)	5·9 (51)
H(N12)	352 (15)	112 (15)	92 (19)	0·2 (79)
H(N31)	161 (6)	274 (6)	−80 (7)	0·2 (17)
H(N32)	114 (10)	248 (10)	0 (13)	5·9 (39)
H(N51)	314 (9)	263 (10)	−139 (12)	3·3 (32)
H(N52)	365 (9)	189 (8)	−124 (11)	2·8 (28)

dispersion of the Co atom for Cu *Kβ* radiation was taken from Hazell (1967).

The following computer programs were used. ALGOL data-reduction programs by F. R. Poulsen & T. la Cour and by R. Grønbæk Hazell of this Department. The X-RAY 63 system (Stewart, 1963). SUNY Buffalo program system collected under the guidance of P. Coppens, including *LINUS*, a modification of *ORFLS* (Busing, Martin & Levy, 1962) by W. C. Hamilton, J. A. Ibers & J. E. Edmonds, and *ORFFE* (Busing, Martin & Levy, 1964). *ORTEP*2 (Johnson, 1965).

Discussion. The structure of 2,2′,2″-triaminotriethylamine trihydrochloride [tren(HCl)$_3$] was determined by Rasmussen & Grønbæk Hazell (1963) and Grønbæk Hazell & Rasmussen (1968) who showed that the four N atoms could hardly accommodate any positive ion in a regular tetrahedron. In Ni(tren)(NCS)$_2$ (Rasmussen, 1959) the N atoms of the tren molecule span four corners of an octahedron, and Jain & Lingafelter (1967) showed that the Cu^{II} ion in Cu(tren)(NCS)$_2$ is

Table 2. *Bond distances* (Å) *and angles* (°)

Standard deviations of the last digits are in parentheses.

Co—N(1)	1·98 (1)	Co—N(4)–C(1)	107·9 (9)
Co—N(3)	1·93 (1)	Co—N(4)–C(3)	105·3 (9)
Co—N(4)	1·92 (1)	Co—N(4)–C(7)	109·8 (8)
Co—N(5)	1·89 (1)	Co—N(1)–C(2)	109·3 (8)
Co—N(2)	1·92 (1)	Co—N(3)–C(6)	111·7 (9)
Co—N(6)	1·93 (1)	Co—N(5)–C(8)	109·5 (8)
N(4)–C(1)	1·52 (2)	N(4)–C(1)–C(2)	108·2 (12)
N(4)–C(3)	1·52 (2)	N(4)–C(3)–C(6)	109·3 (12)
N(4)–C(7)	1·52 (2)	N(4)–C(7)–C(8)	110·2 (11)
C(1)–C(2)	1·49 (2)	C(1)–C(2)–N(1)	111·1 (12)
C(3)–C(6)	1·46 (2)	C(3)–C(6)–N(3)	108·1 (12)
C(7)–C(8)	1·43 (2)	C(7)–C(8)–N(5)	109·2 (13)
C(2)–N(1)	1·51 (2)	Co—N(6)–C(4)	175·6 (12)
C(6)–N(3)	1·49 (2)	Co—N(2)–C(5)	161·1 (13)
C(8)–N(5)	1·48 (2)	N(6)–C(4)–S(1)	178·8 (13)
N(2)–C(5)	1·15 (2)	N(2)–C(5)–S(3)	178·8 (13)
N(6)–C(4)	1·16 (2)	N(7)–C(9)–S(2)	176·2 (21)
N(7)–C(9)	1·14 (2)	N(4)–Co—N(1)	87·1 (5)
C(4)–S(1)	1·61 (2)	N(4)–Co—N(3)	86·7 (5)
C(5)–S(3)	1·60 (2)	N(4)–Co—N(5)	87·0 (5)
C(9)–S(2)	1·63 (2)	N(2)–Co—N(6)	91·9 (6)

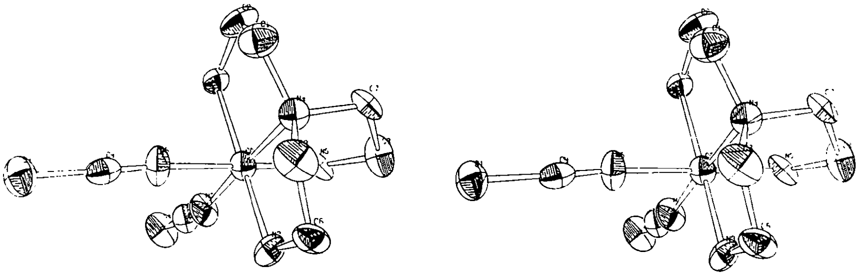

Fig. 1. Stereo drawing of the Co(tren)(NCS)$_2^+$ ion.

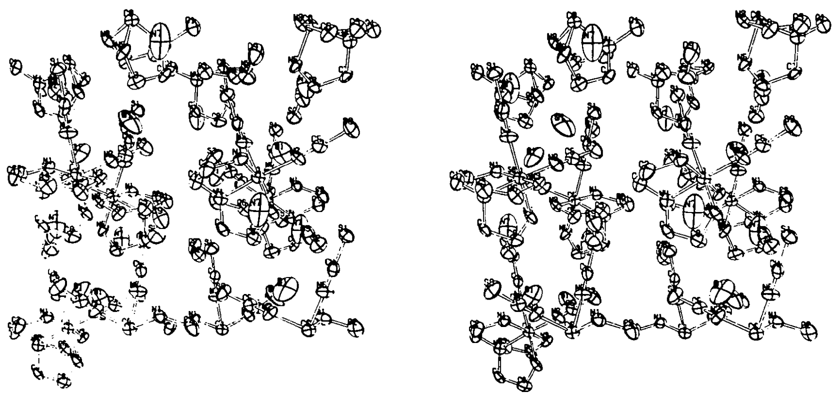

Fig. 2. Stereo view of the contents of the unit cell showing the very large temperature movements of the free thiocyanate ion and the water molecule.

five-coordinated with the N atoms of tren located at four corners of a trigonal bipyramid. The crystal structure of $[Co(tren)(NCS)_2]NCS.H_2O$ 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 $[Coen_2SO_3NCS].2H_2O$ (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].

We thank the IBM Research Foundation at the Northern Europe University Computing Centre for a maintenance grant to F. A. Kundell during 1968–1969, when part of the work reported was carried out; Carlsberg Fondet for providing the linear diffractometer; Videnskabsfondet for providing the Supper–Pace diffractometer; and Mr H. S. Sørensen for preparing the crystals.

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.

Acta Cryst. (1975). B**31**, 2881

Refinement of the Crystal Structure of Nb_5Ge_3

BY SUSAN JAGNER* AND SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

(*Received* 31 *July* 1975; *accepted* 4 *August* 1975)

Abstract. Nb_5Ge_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_5Ge_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_3Ge and Nb_5Ge_3 were both present.

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

---

* Present address: Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, Fack, S-402 20 Göteborg 5, Sweden.