but distinct difference in the Z—Ti—O—C conformations. The conformation of O1=Ti—O3—C18 is antiperiplanar, whereas that of O3—Ti=O1—C11 is almost anticlinal.

BB thanks the Belgian Organization IWONL for a predoctoral grant and YD thanks the Antwerp Provincial Authorities for financial support. This text presents research results of the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State – Prime Minister's Office – Science Policy Programming. The scientific responsibility, however, remains with the authors.

References

Bromilow, J., Brownlee, T. R. C., Craik, D. J., Fiske, P. R., Rowe, J. E. & Sadek, M. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 753–762.
Dang, Y., Geise, H. J., Dommisse, R., Esmans, E. & Desseyn, H. O. (1990). *J. Organomet. Chem.* **381**, 333–348.
Dang, Y., Geise, H. J., Dommisse, R., Nouwen, J. & Gelan, J. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 1785–1790.
Dang, Y., Geise, H. J., Esmans, E., Claereboudt, J. & Claeys, M. (1991). To be published.
Döppert, K., Klein, H.-P. & Thewalt, U. (1986). *J. Organomet. Chem.* **303**, 205–211.
Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Phys. Chem.* **92**, 856–867.
Frenz, B. A. (1978). *The Enraf–Nonius CAD4 SDP–A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.
Hoffman, D. M., Chester, N. D. & Fay, R. C. (1983). *Organometallics*, **2**, 48–52.
Prick, P. A. J. (1979). PhD Thesis, Univ. Nijmegen, The Netherlands.
Seiler, P. & Dunitz, J. D. (1987). *Acta Cryst.* **B35**, 1068–1074.
Talberg, H. J. (1979). *Acta Chem. Scand. Ser. A*, **33**, 289–296.
Verbruggen, M., Yang Zhou, Lenstra, A. T. H. & Geise, H. J. (1988). *Acta Cryst.* **C44**, 2120–2123.

Acta Cryst. (1991). C**47**, 2047–2052

Two Isomeric Chromium(III) Complexes with 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol in One Structure: $[Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)][Cr^{III}(C_6H_{15}N_3O_3)_2]_2(SO_4)_4.30H_2O$

By Helmut W. Schmalle

Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, *CH*-8057 *Zürich, Switzerland*

and Kaspar Hegetschweiler* and Michele Ghisletta

Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 *Zürich, Switzerland*

(*Received* 15 *February* 1991; *accepted* 18 *April* 1991)

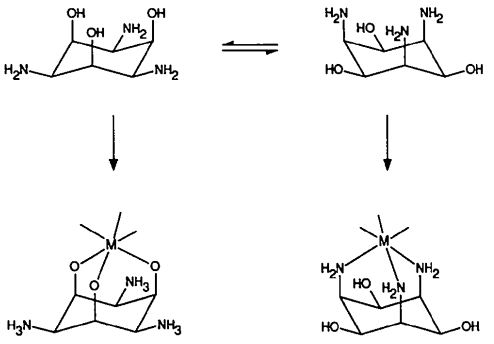
Abstract. $[Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)][Cr^{III}(C_6H_{15}N_3O_3)_2]_2(SO_4)_4.30H_2O$, M_r = 2142·9, triclinic, $P\bar{1}$, a = 10·977 (6), b = 12·754 (2), c = 16·370 (5) Å, α = 94·96 (2), β = 103·22 (4), γ = 94·43 (3)°, V = 2212 (4) Å^3, Z = 1, D_x = 1·608 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·56 mm^{-1}, $F(000)$ = 1139, T = 295 K. The structure was determined by single-crystal X-ray diffraction using 7777 unique reflections and refined by block-diagonal-matrix least-squares calculations to R = 0·063 with 6078 observed $[I > 3\sigma(I)]$ unique reflections. The unit cell contains two $Cr(N_3O_3)$ and one $Cr(O_6)$ coordinating complexes of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, four sulfate groups and 30 water molecules. The average Cr—O distance in the $Cr(O_6)$ complex is 1·983 (4) Å, and 1·943 (3) Å in the $Cr(N_3O_3)$ complex, the average Cr—N distance is 2·089 (5) Å. The structure is predominantly stabilized by hydrogen bonds of the types N—H···O and O—H···O.

Introduction. 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (TACI, $C_6H_{15}N_3O_3$) and its methylated derivatives represent a new class of interesting ligands with high affinity for Fe^{III} (Hegetschweiler, Erni, Schneider & Schmalle, 1990) and have recently been considered for the treatment of Cooley's anaemia (Schneider, Erni & Hegetschweiler, 1989). Owing to the chair–chair interconversion (I) and the possible coordination of the atoms in the ax-eq-ax or ax-ax-ax sequence (II), TACI provides four different metal binding sites [O(2), O(4), O(6)], [N(1), N(3), N(5)] and *e.g.* [N(1), O(2), O(6)] and [O(4), N(3),

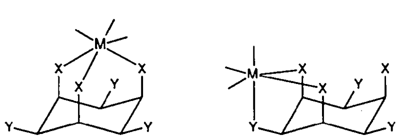
---

* Author to whom correspondence should be addressed.

N(5)], which enables the formation of a large variety of possible isomeric bis complexes. However, nothing is so far known about the structure of metal complexes with TACI. In this contribution, the X-ray diffraction study of a TACI–chromium(III) complex is presented.



(I)



(II)

Experimental. TACI was prepared as described previously (Hegetschweiler, Erni, Schneider & Schmalle, 1990). The chromium complex was obtained by direct reaction of a slight excess of the ligand with Cr^{III}: $KCr(SO_4)_2.12H_2O$ (0·5 g) and TACI (0·4 g) were dissolved in 10 ml of water and the mixture was refluxed for 24 h under N_2. The red solution was filtered and layered with ethanol. Single crystals were obtained which effloresced during drying *in vacuo*. Analysis for the dried product [calculated for $Cr_3(C_6H_{15}N_3O_3)_5(C_6H_{14}N_3O_3)(SO_4)_4.2H_2O$]: C 26·39, H 5·72, N 15·73%; found: C 26·41, H 6·25, N 15·54%.

The crystal structure of the title compound was determined using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. A red crystal of the TACI–Cr^{III} complex of approximate dimensions of 0·44 × 0·30 × 0·30 mm was sealed in a 0·3 mm ∅ glass capillary, including its mother liquor. Unit-cell parameters were determined by least-squares refinement of the setting angles of 25 automatically centred reflections in the range $6·8 < \theta < 10·3°$. Intensities of 8990 reflections (excluding 114 standards) in the interval $-13 < h < 13$, $-15 < k < 15$, $0 < l < 19$ with θ between 1·0 und 26·0° ($\sin\theta_{max}/\lambda = 0·617$ Å^{-1}) were collected using the ω–2θ scan technique with a scan width of $\Delta\omega = (0·80 + 0·35\tan\theta)°$. The scan speed rate varied from 1·50 to 5·49° min^{-1}, the max. measuring time was 50 s. Three standard reflections were monitored every 3 h of measuring time, no loss of intensities was noted. Orientation was controlled every 400 reflections using four standard reflections. 567 reflections had negative intensities and were excluded from the data set. A numerical absorption correction ($\mu = 0·56$ mm^{-1}) based on six indexed crystal faces was applied with *SHELX76* (Sheldrick, 1976); transmission factors ranged between 0·836 and 0·867. Data were corrected for Lorentz and polarization effects. Data reduction led to 7777 unique reflections (1292 reflections averaged, $R_{int} = 0·017$). 6091 reflections were considered observed with $I \geq 3\sigma(I)$, $\sigma(I)$ based on counting statistics, 1686 reflections were unobserved.

The phase problem was solved by Patterson methods with *SHELXS86* (Sheldrick, 1985) in the space group $P\bar{1}$. From a 'chicken-wire' solution the information of eight trial heavy atomic positions ($R_E = 0·067$) with coordinates x,y,z and $0·5 + x,y,z$ was used to restart the Patterson routine in the reduced cell ($a/2$, b, c). From this calculation two Cr atoms and some of the coordinating O and other ligand atoms were considered as part of a correct model and were refined (coordinates $x/2,y,z$) in the large unit cell with isotropic temperature parameters in the non-centrosymmetric space group $P1$. The correct centre of symmetry was deduced by shifting all x coordinates about $+0·25$. Several refinement cycles and subsequent difference Fourier syntheses revealed all non-H-atom positions. 15 water molecules localized in the asymmetric unit were refined with isotropic displacement parameters, while the Cr, C, N, O and S atoms were refined anisotropically. According to the different mean C—N and C—O bond distances of 1·476 (2) and 1·430 (2) Å in the *N,N*-dimethylated TACI molecule (Hegetschweiler *et al.*, 1990) and the observed values of the bond lengths between Cr and the ligand atoms it was noticed during the refinement that Cr(1) was coordinated by three N and three O atoms of two TACI ligands. The second Cr atom was lying at a centre of symmetry and was coordinated by six O atoms of two TACI molecules. As the number of Cr and O atoms was underestimated in the beginning, the absorption correction has been repeated with the completed structural formula. With this data set 75 H-atom positions were localized in the difference Fourier maps, 45 of them belonging to the three ligand molecules. They were refined with fixed isotropic displacement parameters. Considering the charge balance, one of the three complexes must have the charge +2; this can obviously be achieved by the deprotonation of one of the NH_3 groups of one of the ligands. However, since all H-atom positions for the uncoordinated NH_3 groups could be localized in difference Fourier maps, the missing H atom must be statistically distributed over all ligands. At this stage the atoms were separated in two groups and refined with block-diagonal-matrix least-squares calculations with *SHELX76* (Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$, unit weights, on F_{hkl} with anisotropic thermal parameters for the non-H atoms using 307 and 310 variables and 6078 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ based on counting statistics, final $R = 0{\cdot}063$, $wR = 0{\cdot}068$. The final max. shift/e.s.d. was 0·063. The max. and min. heights in the final difference Fourier synthesis were 0·86 and $-0{\cdot}93$ e Å^{-3}. Scattering factors were used as in *SHELX76* and from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 55, 99–102, 149). The refined atomic and equivalent isotropic displacement parameters are listed in Table 1.* The standard deviations of U_{eq} were calculated according to Schomaker & Marsh (1983). Calculations were performed on MicroVAX/VMS 3100 and HDS AS/XL V60 computers. Further programs used: *HIPAS* (Hiller, 1990), *SHELXTL-Plus* (Sheldrick, 1988), *PARST88* (Nardelli, 1988), *ORFFE3* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971).

Discussion. The asymmetric unit contains one $Cr(N_3O_3)$ coordinating complex, one half of a $Cr(O_6)$ coordinating isomer, two sulfate groups and 15 water molecules. The atom-numbering scheme is shown in the *ORTEP* (Johnson, 1971) drawing of Fig. 1(*a*) and 1(*b*), bond distances and angles are given in Table 2. The preference of metal ions for either the ax-eq-ax or the ax-ax-ax site (II) in a variety of polyols has been investigated by Angyal (1974). From NMR spectra, the author postulated that large cations (diameter > 1·6 Å) coordinate to the ax-eq-ax site whereas small cations are bound to the ax-ax-ax site. It should be noted that the observed binding of Cr^{III} (diameter = 1·28 Å) to the two ax-ax-ax sites of TACI is in agreement with this postulatum.

The average Cr—O distances of 1·983 (4) Å in the $Cr(O_6)$ isomer and 1·943 (3) Å in the $Cr(N_3O_3)$ isomer compare well with those found in Cr(acetylacetonato)$_3$: 1·951 (6), *trans*-Cr(benzohydroximato)$_3$]: 1·972 (5), $[Cr(catecholato)_3]^{3-}$: 1·986 (4) (Abu-Dari & Raymond, 1979, and references therein) and $[Cr(oxalato)_3]^{3-}$: 1·972 (5) Å (Golic & Bulc, 1988). The Cr—O distances in the $Cr(N_3O_3)$ isomer are significantly shorter than those in the $Cr(O_6)$ isomer which possibly might be explained by a *trans* influence of the coordinating alkoxo groups. The average Cr—N distances of 2·089 (5) Å are in agreement with those reported in the literature for amine ligands, *e.g.* $[Cr(diaminopropane)_3]^{3+}$: 2·096 (3) or $[Cr(NH_3)_6]^{3+}$: 2·080 (4) Å (Jurnak & Raymond, 1974).

Table 1. *Atomic coordinates and isotropic or equivalent isotropic displacement parameters with e.s.d.'s in parentheses for non-*H *atoms of the* $Cr_3^{III}(TACI)_6(SO_4)_4.30H_2O$ *complex*

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

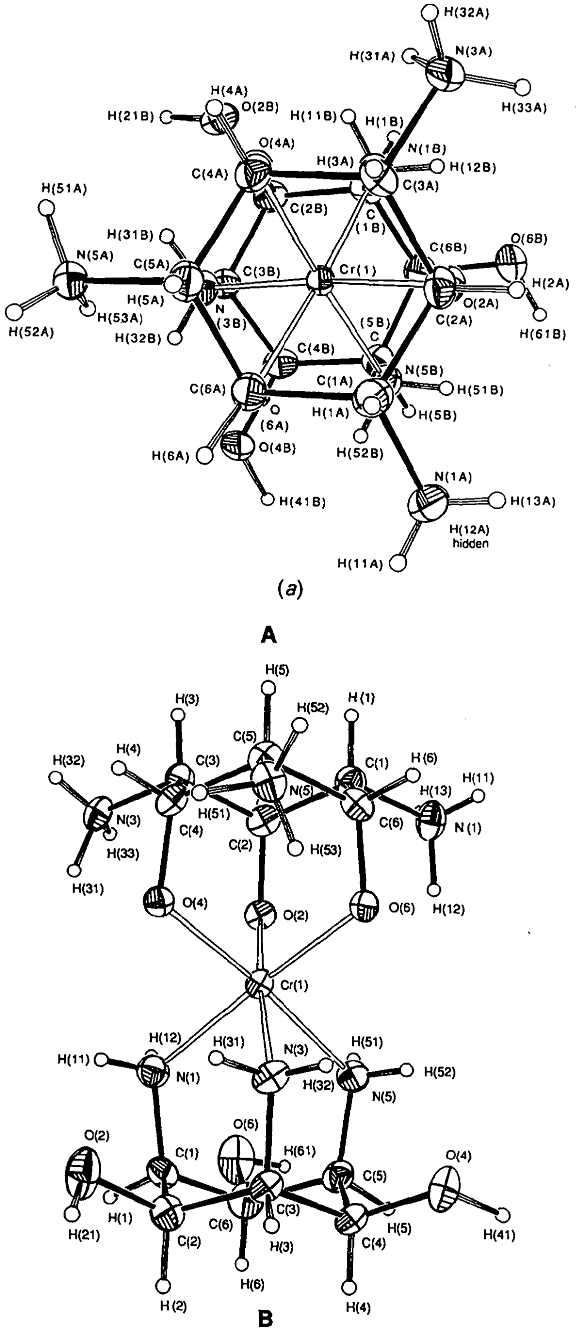
	x	*y*	*z*	U_{eq}/U_{iso}(Å^2)
Cr(1)	0·29570 (7)	0·11737 (6)	0·10291 (5)	0·0161 (2)
O(2*A*)	0·1311 (3)	0·0359 (3)	0·0795 (2)	0·0189 (7)
O(4*A*)	0·3486 (3)	0·0322 (3)	0·0148 (2)	0·0153 (7)
O(6*A*)	0·3678 (3)	0·0288 (3)	0·1878 (2)	0·0194 (7)
N(1*A*)	0·1565 (5)	−0·0830 (4)	0·2246 (3)	0·027 (1)
N(3*A*)	0·1124 (4)	−0·0758 (4)	−0·0813 (3)	0·023 (1)
N(5*A*)	0·5319 (4)	−0·0837 (4)	0·1106 (3)	0·022 (1)
C(1*A*)	0·2042 (5)	−0·1180 (4)	0·1507 (3)	0·021 (1)
C(2*A*)	0·1313 (5)	−0·0748 (4)	0·0712 (3)	0·021 (1)
C(3*A*)	0·1849 (5)	−0·1143 (4)	−0·0026 (3)	0·020 (1)
C(4*A*)	0·3255 (5)	−0·0780 (4)	0·0115 (3)	0·020 (1)
C(5*A*)	0·3949 (5)	−0·1196 (4)	0·0921 (3)	0·021 (1)
C(6*A*)	0·3440 (5)	−0·0812 (4)	0·1682 (3)	0·020 (1)
N(1*B*)	0·2334 (5)	0·2208 (4)	0·0134 (3)	0·024 (1)
N(3*B*)	0·4666 (4)	0·2121 (3)	0·1376 (3)	0·021 (1)
N(5*B*)	0·2380 (4)	0·2185 (3)	0·1913 (3)	0·022 (1)
O(2*B*)	0·4589 (4)	0·3203 (3)	−0·0033 (2)	0·020 (1)
O(4*B*)	0·4641 (3)	0·3260 (3)	0·2906 (2)	0·013 (1)
O(6*B*)	0·0735 (4)	0·3346 (4)	0·0821 (3)	0·023 (1)
C(1*B*)	0·2642 (5)	0·3360 (4)	0·0368 (3)	0·022 (1)
C(2*B*)	0·4063 (5)	0·3652 (4)	0·0616 (3)	0·024 (1)
C(3*B*)	0·4690 (5)	0·3283 (4)	0·1461 (3)	0·020 (1)
C(4*B*)	0·4062 (5)	0·3665 (4)	0·2158 (3)	0·023 (1)
C(5*B*)	0·2641 (5)	0·3346 (4)	0·1919 (3)	0·022 (1)
C(6*B*)	0·2036 (5)	0·3714 (5)	0·1079 (4)	0·028 (1)
Cr(2)	0·5000	0.5000	0·5000	0·0171 (2)
O(2*C*)	0·3616 (3)	0·5859 (3)	0·5162 (2)	0·0211 (7)
O(4*C*)	0·4572 (3)	0·4094 (3)	0·5833 (2)	0·0226 (7)
O(6*C*)	0·3761 (3)	0·4096 (3)	0·4090 (2)	0·0225 (7)
N(1*C*)	0·1611 (5)	0·5312 (4)	0·3652 (3)	0·029 (1)
N(3*C*)	0·3080 (5)	0·5338 (4)	0·6706 (3)	0·026 (1)
N(5*C*)	0·3458 (6)	0·2212 (4)	0·4823 (4)	0·033 (1)
C(1*C*)	0·1807 (5)	0·4664 (4)	0·4372 (3)	0·024 (1)
C(2*C*)	0·2437 (5)	0·5366 (4)	0·5186 (3)	0·024 (1)
C(3*C*)	0·2528 (5)	0·4672 (4)	0·5899 (3)	0·023 (1)
C(4*C*)	0·3320 (5)	0·3747 (4)	0·5796 (3)	0·023 (1)
C(5*C*)	0·2687 (5)	0·3095 (4)	0·4962 (3)	0·025 (1)
C(6*C*)	0·2576 (5)	0·3752 (4)	0·4215 (3)	0·023 (1)
S(1)	0·9104 (1)	0·3135 (1)	0·2409 (1)	0·0299 (3)
O(1)	0·8972 (5)	0·3392 (4)	0·3269 (3)	0·060 (1)
O(2)	0·9771 (4)	0·2182 (3)	0·2356 (3)	0·042 (1)
O(3)	0·9853 (4)	0·4031 (3)	0·2189 (3)	0·047 (1)
O(4)	0·7875 (5)	0·2936 (4)	0·1830 (4)	0·068 (2)
S(2)	0·8280 (1)	0·8414 (1)	0·2262 (1)	0·0334 (3)
O(5)	0·8106 (6)	0·9213 (5)	0·2912 (4)	0·080 (2)
O(6)	0·8772 (7)	0·8969 (5)	0·1652 (4)	0·082 (2)
O(7)	0·7076 (5)	0·7845 (4)	0·1843 (5)	0·091 (2)
O(8)	0·9169 (5)	0·7720 (5)	0·2637 (4)	0·077 (2)
O(*W*1)	0·1519 (5)	0·1118 (4)	0·3392 (3)	0·051 (1)
O(*W*2)	0·9863 (4)	0·3119 (4)	0·5919 (3)	0·050 (1)
O(*W*3)	0·6854 (5)	0·0916 (4)	0·2195 (4)	0·063 (1)
O(*W*4)	0·3662 (5)	0·7890 (4)	0·5315 (3)	0·062 (1)
O(*W*5)	0·3410 (6)	0·4270 (5)	0·8172 (4)	0·074 (2)
O(*W*6)	0·3557 (5)	0·6548 (4)	0·3141 (3)	0·057 (1)
O(*W*7)	0·7049 (5)	0·4180 (4)	0·0519 (3)	0·061 (1)
O(*W*8)	0·3140 (6)	0·8691 (5)	0·3749 (4)	0·079 (2)
O(*W*9)	0·3957 (6)	0·6380 (5)	0·1523 (4)	0·079 (2)
O(*W*10)	0·4658 (5)	0·0562 (4)	0·3588 (3)	0·058 (1)
O(*W*11)	0·1210 (6)	0·8049 (5)	0·5622 (4)	0·087 (2)
O(*W*12)	0·3698 (8)	0·1015 (7)	0·6163 (5)	0·116 (3)
O(*W*13)	0·1221 (6)	0·6201 (5)	0·0485 (4)	0·087 (2)
O(*W*14)	0·0066 (9)	0·6106 (7)	0·1802 (6)	0·133 (3)
O(*W*15)	0·9977 (9)	0·0024 (8)	0·4196 (6)	0·139 (3)

Conformational analysis of the TACI ligands with *PARST88* (Nardelli, 1988) showed chair conformations for the three independent ligands (compare Fig.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, hydrogen-bonding parameters and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54176 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1*b* and Fig. 2). Puckering parameters according to Cremer & Pople (1975) are given in Table 3. The polar positions for the three ligands *A*, *B*, *C* (θ = 179, 178, 1°) are close to 180 or 0°, the theoretical values for undistorted chairs.



(*a*)

(*b*)

Fig. 1. (*a*) *ORTEP* plot with numbering scheme of complex 1 and vibrational ellipsoids at the 50% probability level. (*b*) Complex 1 rotated about 90° around the (non-crystallographic) *y* axis. H atoms are shown as spheres of arbitrary size.

Table 2. *Bond distances* (Å) *and angles* (°) *for* [Cr^{III}(C$_6$H$_{14}$N$_3$O$_3$)(C$_6$H$_{15}$N$_3$O$_3$)][Cr^{III}(C$_6$H$_{15}$N$_3$O$_3$)$_2$]$_2$-(SO$_4$)$_4$.30H$_2$O

Cr(1)—O(2*A*)	1·954 (3)	Cr(1)—N(5*B*)	2·092 (5)
Cr(1)—O(4*A*)	1·950 (4)	Cr(2)—O(2*C*)	1·992 (4) 2 ×
Cr(1)—O(6*A*)	1·934 (3)	Cr(2)—O(4*C*)	1·974 (4) 2 ×
Cr(1)—N(1*B*)	2·090 (5)	Cr(2)—O(6*C*)	1·983 (3) 2 ×
Cr(1)—N(3*B*)	2·085 (4)		

	A	*B*	*C*
C(1)—N(1)	1·474 (8)	1·478 (7)	1·482 (8)
C(1)—C(2)	1·534 (7)	1·527 (7)	1·526 (7)
C(1)—C(6)	1·524 (7)	1·520 (9)	1·527 (8)
C(2)—C(3)	1·525 (8)	1·528 (7)	1·515 (8)
C(2)—O(2)	1·406 (6)	1·420 (7)	1·405 (6)
C(3)—N(3)	1·494 (7)	1·474 (7)	1·480 (7)
C(3)—C(4)	1·535 (7)	1·527 (8)	1·539 (8)
C(4)—C(5)	1·525 (7)	1·531 (7)	1·522 (7)
C(4)—O(4)	1·404 (6)	1·406 (6)	1·397 (6)
C(5)—N(5)	1·492 (7)	1·485 (7)	1·494 (8)
C(5)—C(6)	1·536 (8)	1·515 (8)	1·530 (8)
C(6)—O(6)	1·403 (6)	1·423 (7)	1·405 (7)

S(1)—O(1)	1·459 (6)	S(2)—O(5)	1·465 (7)
S(1)—O(2)	1·472 (5)	S(2)—O(6)	1·449 (7)
S(1)—O(3)	1·474 (5)	S(2)—O(7)	1·447 (5)
S(1)—O(4)	1·451 (5)	S(2)—O(8)	1·437 (6)

O(2*A*)—Cr(1)—O(4*A*)	92·7 (1)	O(2*C*)—Cr(2)—O(4*C*)	88·3 (2)
O(2*A*)—Cr(1)—O(6*A*)	92·3 (1)	O(2*C*)—Cr(2)—O(6*C*)	88·2 (1)
O(4*A*)—Cr(1)—O(6*A*)	92·1 (1)	O(4*C*)—Cr(2)—O(6*C*)	89·6 (1)
N(1*B*)—Cr(1)—O(2*A*)	92·8 (2)	O(2*C*^{i})—Cr(2)—O(4*C*^{i})	88·3 (2)
N(1*B*)—Cr(1)—O(4*A*)	87·7 (2)	O(2*C*^{i})—Cr(2)—O(6*C*^{i})	88·2 (1)
N(1*B*)—Cr(1)—O(6*A*)	174·9 (2)	O(4*C*^{i})—Cr(2)—O(6*C*^{i})	89·6 (1)
N(3*B*)—Cr(1)—O(2*A*)	174·5 (2)	O(2*C*)—Cr(2)—O(4*C*^{i})	91·7 (1)
N(3*B*)—Cr(1)—O(4*A*)	92·7 (2)	O(2*C*^{i})—Cr(2)—O(4*C*)	91·7 (1)
N(3*B*)—Cr(1)—O(6*A*)	87·0 (2)	O(2*C*^{i})—Cr(2)—O(6*C*)	91·7 (1)
N(5*B*)—Cr(1)—O(2*A*)	88·7 (2)	O(2*C*)—Cr(2)—O(6*C*^{i})	91·7 (1)
N(5*B*)—Cr(1)—O(4*A*)	175·4 (2)	O(4*C*)—Cr(2)—O(6*C*^{i})	90·4 (1)
N(5*B*)—Cr(1)—O(6*A*)	92·2 (2)	O(6*C*)—Cr(2)—O(4*C*^{i})	90·4 (1)
N(1*B*)—Cr(1)—N(3*B*)	87·9 (2)	O(2*C*)—Cr(2)—O(2*C*^{i})	180·0
N(1*B*)—Cr(1)—N(5*B*)	87·9 (2)	O(4*C*)—Cr(2)—O(4*C*^{i})	180·0
N(3*B*)—Cr(1)—N(5*B*)	85·9 (2)	O(6*C*)—Cr(2)—O(6*C*^{i})	180·0

Cr(1)—O(2*A*)—C(2*A*)	116·0 (3)	Cr(2)—O(2*C*)—C(2*C*)	120·6 (3)
Cr(1)—O(4*A*)—C(4*A*)	117·0 (3)	Cr(2)—O(4*C*)—C(4*C*)	120·6 (3)
Cr(1)—O(6*A*)—C(6*A*)	118·0 (3)	Cr(2)—O(6*C*)—C(6*C*)	120·0 (3)
Cr(1)—N(1*B*)—C(1*B*)	119·1 (3)	Cr(2)—O(2*C*^{i})—C(2*C*^{i})	120·6 (3)
Cr(1)—N(3*B*)—C(3*B*)	120·3 (3)	Cr(2)—O(4*C*^{i})—C(4*C*^{i})	120·6 (3)
Cr(1)—N(5*B*)—C(5*B*)	119·0 (4)	Cr(2)—O(6*C*^{i})—C(6*C*^{i})	120·0 (3)

	A	*B*	*C*
N(1)—C(1)—C(2)	110·7 (4)	111·1 (4)	109·7 (4)
N(1)—C(1)—C(6)	109·0 (4)	109·6 (5)	110·6 (5)
C(2)—C(1)—C(6)	110·8 (5)	111·2 (4)	111·6 (4)
C(1)—C(2)—C(3)	107·9 (4)	113·0 (5)	106·9 (4)
C(1)—C(2)—O(2)	113·7 (4)	108·5 (4)	112·7 (5)
C(3)—C(2)—O(2)	112·1 (4)	109·9 (4)	112·1 (4)
N(3)—C(3)—C(2)	108·8 (4)	109·9 (4)	108·5 (4)
N(3)—C(3)—C(4)	110·2 (4)	110·9 (5)	110·4 (4)
C(2)—C(3)—C(4)	112·3 (4)	111·3 (4)	112·1 (5)
C(3)—C(4)—C(5)	108·0 (4)	111·8 (4)	107·2 (4)
C(3)—C(4)—O(4)	112·2 (4)	108·5 (4)	112.2 (4)
C(5)—C(4)—O(4)	111·8 (4)	111·4 (5)	112·1 (5)
C(4)—C(5)—C(6)	111·6 (4)	111·2 (5)	112·0 (4)
N(5)—C(5)—C(4)	110·4 (4)	110·2 (4)	108·8 (4)
N(5)—C(5)—C(6)	108·5 (4)	111·4 (4)	108·0 (5)
C(5)—C(6)—C(1)	109·2 (4)	113·7 (5)	107·5 (5)
C(1)—C(6)—O(6)	111·9 (4)	107·6 (4)	112·9 (4)
C(5)—C(6)—O(6)	111·6 (4)	111·4 (5)	111·8 (4)

O(1)—S(1)—O(2)	110·4 (3)	O(5)—S(2)—O(6)	107·2 (4)
O(1)—S(1)—O(3)	108·0 (3)	O(5)—S(2)—O(7)	109·5 (4)
O(1)—S(1)—O(4)	110·2 (3)	O(5)—S(2)—O(8)	109·7 (4)
O(2)—S(1)—O(3)	108·6 (3)	O(6)—S(2)—O(7)	108·8 (4)
O(2)—S(1)—O(4)	108·5 (3)	O(6)—S(2)—O(8)	109·5 (4)
O(3)—S(1)—O(4)	111·1 (3)	O(7)—S(2)—O(8)	112·0 (3)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

Mean torsional angles N$_{eq}$—C—C—O$_{ax}$ in ligand *A* are −55·9 (6) and 54·3 (6)°, similar to those calculated for ligand *C* with −57·4 (6) and 56·9 (6)°. They are slightly different from the torsional angles N$_{ax}$—

Table 3. *Puckering parameters Q* (Å), *φ and θ* (°) *for the atoms* C(1) *to* C(6) *of the TACI ligands A, B and C*

	A	*B*	*C*
*Q*2	0·0102	0·0197	0·0132
*Q*3	−0·6076	−0·5385	0·6194
Q	0·608	0·539	0·620
φ	−133·0	−0·60	43·5
θ	179·03	177·90	1·22

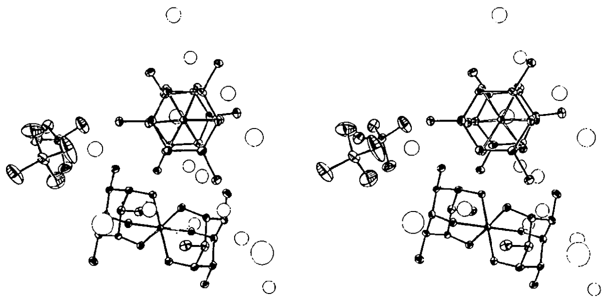


Fig. 2. *ORTEP* (Johnson, 1971) stereo plot including complex 2, sulfate groups and water molecules.

C—C—O$_{eq}$ in ligand *B*, where the N atoms coordinate to Cr(1), mean values are −51·8 (6) and 52·7 (6)°.

The structure can be described as a layered structure with *A*,*B*,*A*,*B*,*A*... layers perpendicular to the *c** axis: complex Cr(1) and sulfate groups form *A* layers in the *ab* plane along **a**, with *z* coordinates approximately around 0·0+/−0·30. Complex Cr(2) is rotated about 90°.

The structure can be described as a layered structure with *A*,*B*,*A*,*B*,*A*... layers perpendicular to the *c** axis: complex Cr(1) and sulfate groups form *A* layers in the *ab* plane along **a**, with *z* coordinates approximately around 0·0+/−0·30. Complex Cr(2) is rotated about 90° compared to complex Cr(1) (see Fig. 2) and is running along **a** too, with *z* coordinates being around 0·5+/−0·25, forming *B* layers in the *ab* plane. The layers are connected *via* hydrogen bonds of the types N—H···O and O—H···O. Hydrogen bonds are given in Table 4, the content of the unit cell is shown in the *SHELXTL* (Sheldrick, 1988) stereo plot of Fig. 3. The space between the complexes and sulfate groups is filled with water molecules which also contribute to the stability of the structure by forming hydrogen bonds. Without its mother liquor the crystals decompose within a minute loosing most of the crystal water; only two water molecules remain, according to elemental analysis.

We thank Erwin Herzog for the preparation of the Cr–TACI complex and the ETHZ for financial support (Kredite für Unterricht und Forschung, No. 0.330.089.12/9). Gratitude is expressed to Professor Walter Schneider for helpful discussions.

Table 4. *Hydrogen-bonding contacts* (Å, °) *in* $[\mathrm{Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)}]$-$[\mathrm{Cr^{III}(C_6H_{15}N_3O_3)_2}]_2\mathrm{(SO_4)_4.30H_2O}$

X—H···*Y*	*X*—H	H···*Y*	*X*···*Y*	*X*—H···*Y*
N(1*A*)—H(11*A*)···O(*W*8$^{\rm i}$)	0·81 (6)	2·04 (6)	2·810 (8)	158 (6)
N(1*A*)—H(12*A*)···O(*W*1$^{\rm ii}$)	1·04 (6)	2·17 (6)	2·992 (7)	134 (5)
N(1*A*)—H(13*A*)···O(6$^{\rm iii}$)	0·81 (6)	2.19 (6)	2·980 (9)	166 (6)
N(3*A*)—H(31*A*)···O(6$^{\rm iv}$)	1·01 (6)	1·95 (6)	2·771 (9)	136 (4)
N(3*A*)—H(32*A*)···O(2$^{\rm v}$)	0·82 (6)	2·19 (6)	2·905 (6)	145 (5)
N(3*A*)—H(33*A*)···O(2*A*$^{\rm vi}$)	0·94 (7)	1·83 (7)	2·765 (6)	176 (5)
N(5*A*)—H(51*A*)···O(4*A*$^{\rm v}$)	0·94 (7)	1·85 (7)	2·775 (6)	167 (5)
N(5*A*)—H(52*A*)···O(7$^{\rm i}$)	0·90 (6)	1·92 (6)	2·791 (8)	164 (5)
N(5*A*)—H(53*A*)···O(*W*3$^{\rm ii}$)	0·89 (6)	2·18 (6)	2·893 (7)	137 (5)
N(5*B*)—H(51*B*)···O(2$^{\rm vii}$)	0·86 (6)	2·34 (7)	3·111 (7)	149 (5)
O(2*B*)—H(21*B*)···O(*W*7$^{\rm ii}$)	0·96 (4)	1·87 (5)	2·798 (7)	164 (3)
O(4*B*)—H(41*B*)···O(6*C*$^{\rm ii}$)	1·02 (4)	1·53 (4)	2·547 (5)	171 (2)
O(6*B*)—H(61*B*)···O(3$^{\rm vii}$)	0·90 (5)	1·86 (5)	2·739 (7)	165 (3)
N(1*C*)—H(11*C*)···O(3$^{\rm vii}$)	0·82 (6)	2·17 (6)	2·975 (6)	169 (7)
N(1*C*)—H(12*C*)···O(*W*6$^{\rm ii}$)	0·90 (7)	2·02 (7)	2·876 (8)	158 (6)
N(1*C*)—H(13*C*)···O(*W*2$^{\rm viii}$)	0·99 (6)	1·84 (6)	2·809 (8)	169 (6)
N(3*C*)—H(31*C*)···O(4*B*$^{\rm viii}$)	0·93 (6)	1·98 (6)	2·872 (9)	158 (6)
N(3*C*)—H(32*C*)···O(*W*5$^{\rm ii}$)	0·81 (7)	2·02 (7)	2·827 (9)	176 (5)
N(3*C*)—H(33*C*)···O(1$^{\rm viii}$)	0·87 (7)	2·03 (7)	2·880 (8)	165 (5)
N(5*C*)—H(51*C*)···O(*W*4$^{\rm viii}$)	1·05 (6)	2·33 (7)	3·232 (9)	144 (4)
N(5*C*)—H(52*C*)···O(*W*1$^{\rm ii}$)	0·85 (6)	2·15 (5)	2·943 (7)	155 (6)
N(5*C*)—H(53*C*)···O(*W*12$^{\rm ii}$)	0·70 (7)	2·05 (7)	2·755 (11)	177 (7)
O(*W*1)—H(*W*11)···O(2$^{\rm vii}$)	0·93 (6)	1·90 (6)	2·777 (7)	156 (6)
O(*W*2)—H(*W*22)···O(8$^{\rm ix}$)	0·94 (6)	1·79 (6)	2·707 (8)	167 (6)
O(*W*4)—H(*W*42)—O(*W*11$^{\rm ii}$)	0·54 (7)	2·35 (7)	2·868 (9)	162 (8)
O(*W*5)—H(*W*52)···O(*W*9$^{\rm viii}$)	0·67 (7)	2·36 (6)	3·012 (9)	167 (5)
O(*W*7)—H(*W*72)···O(4$^{\rm ii}$)	1·16 (5)	1·72 (6)	2·805 (8)	154 (4)
O(*W*8)—H(*W*82)···O(*W*4$^{\rm ii}$)	1·19 (6)	1·85 (6)	2·796 (8)	133 (4)
O(*W*9)—H(*W*91)···O(*W*6$^{\rm ii}$)	0·86 (7)	1·95 (6)	2·775 (7)	156 (5)
O(*W*9)—H(*W*92)···O(*W*5$^{\rm viii}$)	0·82 (6)	2·25 (6)	3·012 (9)	155 (5)
O(*W*10)—H(101)···O(6*A*$^{\rm ii}$)	1·05 (6)	1·74 (5)	2·741 (6)	157 (5)
O(*W*10)—H(102)···O(*W*4$^{\rm viii}$)	0·99 (5)	1·91 (5)	2·799 (6)	148 (5)
O(*W*13)—H(132)···O(*W*14$^{\rm ii}$)	0·91 (7)	1·88 (7)	2·75 (1)	158 (5)
O(*W*15)—H(152)···O(*W*11$^{\rm viii}$)	0·55 (6)	2·34 (6)	2·89 (1)	173 (8)

Symmetry code: (i) $x, -1+y, z$; (ii) x, y, z; (iii) $-1+x, -1+y, z$; (iv) $1-x, 1-y, -z$; (v) $1-x, -y, -z$; (vi) $-x, -y, -z$; (vii) $-1+x, y, z$; (viii) $1-x, 1-y, 1-z$; (ix) $2-x, 1-y, 1-z$.

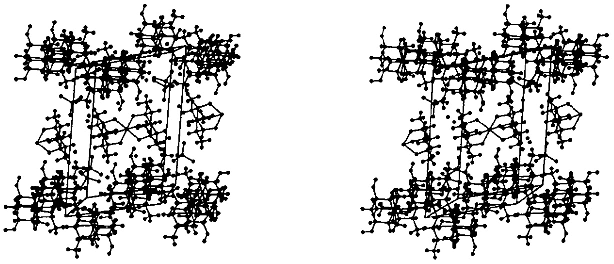


Fig. 3. Stereoview showing the packing diagram of the unit cell approximately in the **b** direction.

References

Abu-Dari, K. & Raymond, K. N. (1979). *Inorg. Chem.* **19**, 2034–2040.

Angyal, S. J. (1974). *Tetrahedron*, **30**, 1695–1702.

Busing, W. R., Martin, K. O., Levy, H. A., Brown, G. M., Johnson, C. K. & Thiessen, W. A. (1971). *ORFFE*3. Report ORNL-TM-306, revised. Oak Ridge National Laboratory, Tennessee, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

GOLIC, L. & BULC, N. (1988). *Acta Cryst.* C**44**, 2065–2068.
HEGETSCHWEILER, K., ERNI, I., SCHNEIDER, W. & SCHMALLE, H. (1990). *Helv. Chim. Acta*, **73**, 97–105.
HILLER, W. (1990). *HIPAS*. Program generates input files and *hkl* files for *SHELXS*86 and *SHELX*76. Univ. of Tübingen, Germany.
JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
JURNAK, F. & RAYMOND, K. N. (1974). *Inorg. Chem.* **13**, 2387–2397.
NARDELLI, M. (1988). *PARST*88. Program for crystallographic calculations. Univ. of Parma, Italy.
SCHNEIDER, W., ERNI, I. & HEGETSCHWEILER, K. (1989). European Patent EP 0 190 676 B1.
SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* A**39**, 819–820.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD. Oxford Univ. Press.
SHELDRICK, G. M. (1988). *SHELXTL-Plus*88. *Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1991). C**47**, 2052–2054

Structure of Bis(thiocyanato-*N*)bis(thiosemicarbazide-*N*^{1},*S*)nickel(II): a Redetermination

BY N. R. SREENIVASA KUMAR, M. NETHAJI AND K. C. PATIL*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, *India*

(*Received* 15 *June* 1990; *accepted* 28 *November* 1990)

Abstract. $[Ni(NCS)_2(CH_5N_3S)_2]$, $M_r = 356·7$, monoclinic, $P2_1/c$, $a = 5·297\ (1)$, $b = 7·869\ (1)$, $c = 16·078\ (2)$ Å, $\beta = 91·53\ (1)°$, $V = 669·9$ Å^3, $Z = 2$, $D_m = 1·76$, $D_x = 1·771$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 19·9$ cm^{-1}, $F(000) = 364$, $T = 295$ K, final $R = 0·026$ for 1576 significant $[F > 10\sigma(F)]$ reflections. The complex lies on a crystallographic centre of symmetry. The Ni atom is octahedrally coordinated by two thiocyanates (through N atoms) and by two thiosemicarbazide molecules (through hydrazinic N and S atoms). The crystal structure is stabilized by N—H···S hydrogen bonds. Early work on this structure [Garaj & Dunaj-Jurco (1968). *Chem. Commun.* p. 518] used photographic data and was refined to $R = 0·13$ for 512 reflections.

Introduction. Metal complexes of the thiosemicarbazide (TSC) molecule have been widely studied because of their broad pharmacological activity (Akbar Ali & Livingstone, 1974; Campbell, 1975). The activity of TSC and related species is thought to be dependent on metal–chelate formation and has led to the study of a large number of nickel(II) complexes (*e.g.* Lopez-Castro & Truter, 1963). Preparation and magnetic properties (Sirota, Sramko & Kohout, 1966) and structure (Garaj & Dunaj-Jurco, 1968) have previously been reported for the title compound. However, the structure is imprecise ($R = 0·13$) as the data were recorded photographically (512 reflections). We report here a redetermination based on diffractometer data.

Experimental. The title compound was prepared by decomposing $N_2H_5Ni(N_2H_3COO)_3.H_2O$ (Braibanti, Bigliardi, Lanfredi & Tiripicchio, 1966) in aqueous thiocyanic acid; D_m measured by flotation using a mixture of chloroform and bromoform. Dark blue

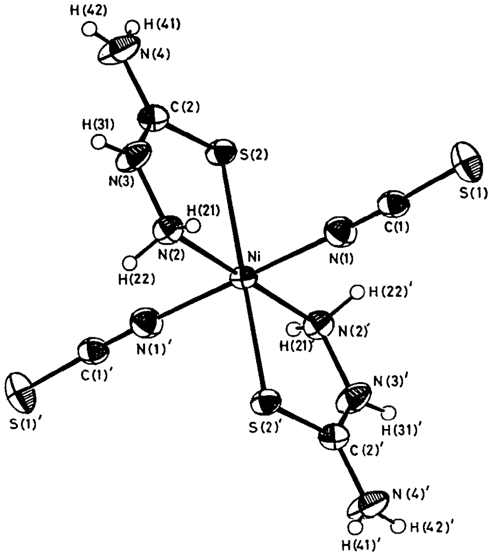


Fig. 1. *ORTEP*II diagram (Johnson, 1976) and atom-numbering scheme. Non-H ellipsoids at 50% probability level. H atoms given arbitrary radii.

---

* To whom correspondence should be addressed.

0108-2701/91/102052-03$03.00