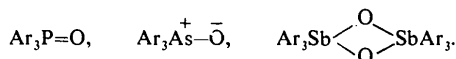


Fig. 1. Perspective view of molecule (1), showing the atom-numbering scheme.

The molecules comprise centrosymmetric dimers: the two crystallographically independent molecules show only trivial structure differences (Table 2). Each Sb atom exhibits rather exact trigonal-bipyramidal coordination with one O atom apical and one equatorial, as expected for a four-membered ring. For Sb(1), the apical atoms are C(121) and O(1') and the equatorial atoms are C(111), C(131) and O(1): of the three Sb—C distances, the apical Sb(1)—C(121) distance is significantly longer than the other two; likewise the apical Sb—O distance is much longer than the corresponding equatorial distance. These observations on $(\text{Ph}_3\text{SbO})_2$ neatly encapsulate most of the familiar generalizations

made by VSEPR theory about trigonal-bipyramidal structures.

The dimeric structure found for triphenylstibine oxide is in sharp contrast to the monomeric structure, containing near-tetrahedral Sb, found for triphenylstibine sulfide (Pebler, Weller & Dehnicke, 1982). It is interesting to note the changes in structure of the triaryl element oxides Ar_3MO ($M = \text{P}, \text{As}$ or Sb) which may most simply be summarized thus:



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Bis(isothiocyanato)(2,2',2''-trihydroxytriethylamine-*N,O,O',O''*)nickel(II)

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Abstract. $[\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_{15}\text{NO}_3)]$, $M_r = 324.06$, monoclinic, $P2_1/c$, $a = 9.4048$ (10), $b = 10.4130$ (7), $c =$

14.0647 (16) Å, $\beta = 101.05$ (1)°, $V = 1351.9$ (3) Å³, $Z = 4$, $D_x = 1.59$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54051$ Å, $\mu = 49.34$ cm⁻¹, $F(000) = 672$, $T = 290$ K. Final $R = 0.034$ for 2234 'observed' reflections and 192 variables. Ni^{2+} is octahedrally coordinated ($\text{NiN}_2\text{O}_3\text{N}$ chromophore) by the N atoms of the NCS^- ions (in mutually

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cis positions) and the N and the O atoms of the quadridentate 2,2',2''-trihydroxytriethylamine ligand. The five-membered rings Ni–N(3)–C(4)–C(3)[C(3')]–O(1), Ni–N(3)–C(5)–C(6)–O(2) and Ni–N(3)–C(7)–C(8)–O(3) adopt envelope conformations. The complex has pseudo- C_s symmetry with Ni, N(3), O(1), N(2) and N(1) defining a pseudo-mirror plane. C(3) is disordered in two pseudo-mirror-related positions [occupancy: 0.65 (1):0.35 (1)]. Intermolecular OH...S and OH...O hydrogen bonds occur.

Introduction. In continuation of our studies of metal complexes of amino alcohols (Sanni, Lenstra & Patel, 1985), we have determined the crystal structure of the title compound. Although the Ni complex of 2,2',2''-triaminotriethylamine has been studied (Rasmussen, 1959) the crystal structure of the Ni complex of 2,2',2''-trihydroxytriethylamine has, to the best of our knowledge, not been reported.

Experimental. The title compound was prepared by heating a mixture of 20 g of hydrated nickel(II) perchlorate and 10 cm³ of 2,2',2''-trihydroxytriethylamine with constant stirring for a few minutes. The resultant green viscous liquid was cooled, dissolved in 80 cm³ of distilled water and filtered. 15 g sodium thiocyanate dissolved in 50 cm³ of distilled water was added to the above filtrate. Green crystals of the title compound separated out after a few hours. Crystallization was from hot methanol. Elemental analysis confirmed the identity of the complex {found: Ni 18.17, C 29.62, H 4.65, S 19.74, N 13.00%; calculated for [Ni(NCS)₂(C₆H₁₅NO₃)]: Ni 18.13, C 29.66, H 4.63, S 19.77, N 12.97%}.

A green crystal of approximately 0.20 × 0.10 × 0.23 mm was used for the measurements. Cu K α radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections with $21 \leq \theta \leq 49^\circ$. The intensity data of 8395 reflections up to $\theta = 70^\circ$ in the range $-11 \leq h \leq 5$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$ were measured, using the ω - 2θ -scan technique with a scan angle of 1.50° and a variable scan rate with a maximum scan time of 15 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min; the final drift-correction factors were between 1.00 and 1.04. Profile analysis was performed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978); an empirical absorption correction was applied using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0.949 to 0.999 with an average of 0.976). Symmetry-equivalent reflections were averaged, $R_{int} = \sum(I - \langle I \rangle) / \sum I = 0.032$, resulting in 2567 unique reflections of which 2234 were observed with $I > 3\sigma(I)$. Lorentz and

polarization corrections were applied and the data were reduced to $|F_o|$ values.

Using the program PATSYS (Behm & Beurskens, 1985), the position of the Ni atom was located from the Patterson map, and automatically input into DIRDIF (Beurskens *et al.*, 1982). The positions of the non-H atoms were located in one DIRDIF run. Isotropic least-squares refinement, using SHELX76 (Sheldrick, 1976), converged at $R = 0.110$. At this stage an additional empirical absorption correction was applied (Walker & Stuart, 1983), leading to a further reduction of R to 0.101 (relative correction factors were in the range 0.813–1.303 with an average of 0.996). The anisotropic refinement led to abnormally high anisotropy for C(3) indicating disorder involving this atom. A Fourier synthesis showed two alternative positions, to be denoted C(3) and C(3'); least-squares refinement led to occupation factors 0.65 and 0.35, respectively. The two disordered sites are pseudo-mirror-related by a plane through O(1)–Ni–N(3)–C(4). All H atoms {except those of C(3)[C(3')]} were located from a difference Fourier synthesis; those of C(3)[C(3')] were fixed at expected positions.

During the final stages of the refinement all positional parameters {except those of H atoms of C(3)[C(3')]}, the anisotropic temperature factors of all non-H atoms (except those of the disordered atom, which was refined with one common isotropic temperature factor for both sites) and the occupation factor for C(3) were refined. The H atoms had a fixed isotropic temperature factor, $U_{iso} = 0.060 \text{ \AA}^2$. The final conventional agreement factors are $R = 0.034$ and $wR = 0.044$ for the 2234 'observed' reflections and 192 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.003F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift over e.s.d. ratio in the final full-matrix least-squares cycle was less than 0.10 for all atoms. The minimum and maximum electron densities in the final difference Fourier map were -0.35 and $+0.20 \text{ e \AA}^{-3}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Plots were made with PLUTO (Motherwell, 1976) and geometrical calculations with PARST (Nardelli, 1983).

Discussion. Final positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1;* selected molecular-geometry data are in Table 2. A stereoview of the molecule showing the crystallographic numbering scheme is given in Fig. 1,

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, all bond distances and angles, torsion angles and puckering parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43556 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
Ni	0.62509 (4)	0.16371 (3)	0.21339 (3)	2.77 (1)
S(1)	0.71843 (8)	0.58325 (7)	0.10138 (6)	5.04 (1)
S(2)	0.17257 (7)	0.11804 (7)	-0.00193 (5)	4.54 (1)
O(1)	0.62801 (24)	-0.02073 (19)	0.26899 (17)	5.29 (7)
O(2)	0.51885 (20)	0.24344 (19)	0.32137 (13)	3.73 (5)
O(3)	0.79042 (21)	0.11807 (21)	0.13615 (13)	4.33 (6)
N(1)	0.63967 (28)	0.34621 (21)	0.16682 (18)	4.26 (7)
N(2)	0.44489 (27)	0.12506 (24)	0.11678 (17)	4.54 (7)
N(3)	0.80415 (22)	0.17858 (19)	0.32536 (14)	3.15 (6)
C(1)	0.67113 (26)	0.44449 (24)	0.14018 (17)	3.38 (7)
C(2)	0.33379 (27)	0.12196 (22)	0.06717 (17)	3.27 (7)
C(3)†	0.7618 (5)	-0.0578 (5)	0.3207 (3)	4.60 (9)
C(3')‡	0.7036 (9)	-0.0376 (8)	0.3602 (6)	4.60 (9)
C(4)	0.8337 (3)	0.0549 (3)	0.37803 (21)	4.64 (9)
C(5)	0.7680 (3)	0.2825 (3)	0.38861 (20)	4.31 (9)
C(6)	0.6191 (3)	0.2628 (4)	0.41172 (20)	4.96 (10)
C(7)	0.9258 (3)	0.2176 (3)	0.27786 (20)	3.89 (8)
C(8)	0.9339 (3)	0.1295 (3)	0.19363 (22)	4.66 (9)

† Occupancy 0.648 (6).

‡ Occupancy 0.352 (6).

Table 2. Selected geometrical data (with e.s.d.'s)

(a) Bond distances (\AA) and angles ($^\circ$) for Ni coordination				
Ni—O(1)	2.072 (2)	Ni—N(1)	2.023 (2)	
Ni—O(2)	2.140 (2)	Ni—N(2)	2.000 (2)	
Ni—O(3)	2.115 (2)	Ni—N(3)	2.079 (2)	
O(1)—Ni—O(2)	93.8 (1)	O(1)—Ni—O(3)	91.6 (1)	
O(1)—Ni—N(1)	174.9 (1)	O(1)—Ni—N(2)	91.0 (1)	
O(1)—Ni—N(3)	80.4 (1)	O(2)—Ni—O(3)	160.3 (1)	
O(2)—Ni—N(1)	86.3 (1)	O(2)—Ni—N(2)	96.3 (1)	
O(2)—Ni—N(3)	81.6 (1)	O(3)—Ni—N(1)	86.7 (1)	
O(3)—Ni—N(2)	102.5 (1)	O(3)—Ni—N(3)	80.6 (1)	
N(1)—Ni—N(2)	94.0 (1)	N(1)—Ni—N(3)	94.6 (1)	
N(2)—Ni—N(3)	171.0 (1)			
(b) Selected torsion angles ($^\circ$) for Ni-2,2',2''-trihydroxytriethylamine coordination				
C(3)—O(1)—Ni—N(3)	-22.5 (3)	C(6)—O(2)—Ni—N(3)	-1.2 (2)	
C(3')—O(1)—Ni—N(3)	18.9 (4)	O(2)—Ni—N(3)—C(5)	-25.2 (2)	
O(1)—Ni—N(3)—C(4)	1.1 (2)			
		C(8)—O(3)—Ni—N(3)	-4.4 (2)	
		O(3)—Ni—N(3)—C(7)	29.2 (2)	
(c) Intermolecular hydrogen bonds				
Donor—H...Acceptor	D—H	D...A	H...A	D—H...A
O(1)—H(1)...O(2)	0.80 (4) \AA	2.980 (3) \AA	2.19 (4) \AA	168 (4) $^\circ$
O(2)—H(2)...S(1)	0.73 (4)	3.142 (2)	2.43 (5)	166 (4)
O(3)—H(3)...S(2)	0.92 (4)	3.159 (2)	2.29 (5)	158 (3)

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y, -z$.

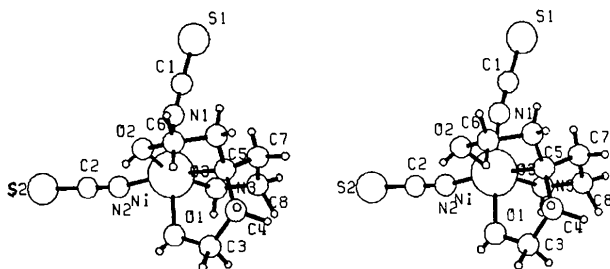


Fig. 1. Stereoview of the molecule with atomic numbering.

the alternative disordered position for C(3) having been removed. The Ni²⁺ ion is octahedrally coordinated by the N atoms of the two NCS⁻ ions (in mutually *cis* positions) and the N and O atoms of the 2,2',2''-trihydroxytriethylamine molecule acting as a quadridentate ligand. A similar unit was reported for bis(isothiocyanato)(2,2',2''-triaminotriethylamine)-nickel(II) (Hall & Woulfe, 1958). The complex has pseudo-C_s symmetry, with Ni, N(3), O(1), N(2) and N(1) defining a pseudo-mirror plane, which also approximately relates the two disordered positions C(3) and C(3'). Endocyclic torsion angles and the Cremer & Pople (1975) puckering parameters have been deposited.* The three five-membered rings Ni—N(3)—C(4)—C(3)[C(3')]—O(1), Ni—N(3)—C(5)—C(6)—O(2) and Ni—N(3)—C(7)—C(8)—O(3) adopt envelope conformations. The planes O(2)—Ni—N(3) and O(3)—Ni—N(3) are almost parallel [dihedral angle 8.55 (8) $^\circ$] and the O(1)—Ni—N(3) plane is almost perpendicular to these planes [dihedral angles 95.32 (8) and 93.23 (8) $^\circ$, respectively].

The Ni—N—C—S groupings are close to linear [angles between Ni—N and essentially linear N—C—S groups 11.99 (9) and 12.24 (8) $^\circ$, respectively], as was found for bis(isothiocyanato)(2,2',2''-triaminotriethylamine)nickel(II) (Hall & Woulfe, 1958), but this is contrary to the results reported by Rasmussen (1958). The Ni—N bonds for coordinated NCS⁻ ions are almost perpendicular to each other [angle 94.0 (1) $^\circ$] and lie almost in the O(1)—Ni—N(3) plane [line-to-plane angles 0.86 (9) and 2.77 (7) $^\circ$ for Ni—N(1) and Ni—N(2)]. The Ni—N(3) bond distance, 2.079 (2) \AA , is comparable to the value of 2.11 (2) \AA reported for bis(isothiocyanato)(2,2',2''-triaminotriethylamine)-nickel(II) (Cradwick & Hall, 1970), while the Ni—N(isothiocyanato) distances are shorter in the present compound [2.023 (2) and 2.000 (2) \AA against 2.12 (3) and 2.05 (2) \AA]. The Ni—O bond distances compare favourably with the value of 2.096 (1) \AA reported for bis(3-aminopropanol-*O,N*)bis(isothiocyanato)-nickel(II) (Sanni *et al.*, 1985). Details of the intermolecular hydrogen bonding involving O and S atoms are also given in Table 2.

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* See deposition footnote.

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Structure du Di- μ -chloro-bis[triaquachloronickel(II)]–Dichlorure de Pipérazine

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Abstract. $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6] \cdot \text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^-$, $M_r = 526.38$, triclinic, $P\bar{1}$, $a = 6.606$ (3), $b = 8.821$ (2), $c = 8.933$ (2) Å, $\alpha = 110.11$ (2), $\beta = 98.50$ (3), $\gamma = 105.35$ (3)°, $V = 454.6$ Å³, $Z = 1$, $D_x = 1.922$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 29.9$ cm⁻¹, $F(000) = 268$, $T = 295$ K. This crystal structure has been investigated by X-ray diffraction and refined to an R factor of 1.7% for 2250 independent reflections. The structure consists of groups of two edge-sharing $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6]$ octahedra, piperazinium $\text{C}_4\text{H}_{12}\text{N}_2^{2+}$ cations and isolated Cl^- ions: the packing structure is partly ensured by (O or N)–H...Cl hydrogen bonds. The centrosymmetric piperazine molecule adopts the chair form. The Ni...Ni distance in the dimer is 3.480 (1) Å.

Introduction. L'étude de la structure du complexe de pipérazine $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{Cu}_2\text{Cl}_6^{2-}$ (Daoud, Ben Salah, Chappert, Renard, Cheikhrouhou, Tran Qui & Verdager, 1986) a montré que l'ion magnétique Cu^{2+} se trouve dans des sites bipyramidaux formant des chaînes infinies d'ions CuCl_3 . La variation de la susceptibilité de ce composé en fonction de la température montre que son comportement s'explique parfaitement en terme d'un ordre de type antiferromagnétique unidimen-

sionnel de l'ion Cu^{2+} avec $S = \frac{1}{2}$. Ce type de matériaux est actuellement très recherché pour leurs propriétés magnétiques (composés unidimensionnels, verres de spin, etc...). La pipérazine constitue également un ligand d'une grande importance dans les halogénures doubles de métaux de transition.

Dans le cadre d'une étude générale des interactions d'ions magnétiques dans les complexes organo-métalliques (Cu, Ni, Co etc...), nous avons fait la synthèse de cristaux d'un nouveau complexe de pipérazine avec le nickel $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6] \cdot \text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^-$. Nous rapportons ici l'étude structurale de ce composé.

Partie expérimentale. Préparation du dichlorure de pipérazine. Le mélange stœchiométrique d'une mole de pipérazine dissoute dans l'éthanol avec deux moles d'acide chlorhydrique conduit aisément au dichlorure de pipérazine $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^-$. Ce sel doit être lavé plusieurs fois avec l'éther anhydre et conservé à l'abri de l'humidité.

Préparation du complexe du nickel. Le chlorure de nickel hydraté $\text{NiCl}_2 \cdot 3\text{H}_2\text{O}$ et le dichlorure de pipérazine $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^-$, pris dans le rapport