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Synthesis, Spectroscopy, Magnetism and X-ray Structure of Bis(dichloromercury(II)-μ-Cl)mercury Bis[tris(2-aminoethanethiolato)niccolate(II)] Tetrahydrate

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Abstract

The synthesis and 3D-structure are described of an unusual mixed-metal compound with formula $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$, in which aet = the dehydronated 2-aminoethanethiol ligand.

The compound consists of the anionic species $[Ni(aet)_3]^-$ held together in a network with $(Hg_3Cl_4)^{2+}$ ions, via bridging thiolato groups. The chloride ions are only coordinated to the mercury ions. The title compound crystallized in the space group $C2/n$ with $a = 20.076(5)$, $b = 8.513(3)$, $c = 19.964(5)$ Å, $\beta = 93.73(2)°$ and $Z = 4$.

The coordination of Ni(II) is octahedral, whereas the mercury ions are tetrahedrally coordinated. Ni–N distances are 2.088(7)–2.120(8) Å and Ni–S distances are 2.413(2)–2.473(3) Å. Each Hg(II) is involved in a HgS_2Cl_2 chromophore, forming a V-shaped trinuclear cluster Cl–Hg–Cl–Hg–Cl–Hg. Hg–S distances vary from 2.378(2) to 2.388(2) Å and the Hg–Cl bonds range from 2.832(2) to 2.924(2) Å. Bond angles around Ni(II) vary from 83.9(2)° to 95.6(1)°, whereas the bond angles around Hg(II) vary from 90.3(8)° to 153.1(1)°. The ligand field spectrum of Ni(II) agrees with the chromophore *vic*-NiN_3S_3.

Introduction

The diamagnetic bidentate chelate bis(2-aminoethanethiolato)nickel(II) may form heterometallic complexes using the thiolate ligand as a bridging atom. It is interesting to study the magnetic properties of these complexes to find out possible exchange through the diamagnetic Ni(II). In 1984 Blinn *et al.* [1] tried to characterize, among others, a complex they described by the formula $[Hg(Ni(aet)_2)_2]HgCl_4$. They obtained a bright red precipitate with paramagnetic properties. The electronic spectrum was consistent with a six coordinate environment around the nickel(II) ions. The infrared spectra indicated that the compound did not contain the $HgCl_4{}^{2-}$ anion. The magnetic susceptibility was measured and the complex was found to be ferromagnetic in character. Blinn *et al.* [1] stated that the magnetic data appeared anomalous in that the metallo-ligand, $Ni(aet)_2$, is diamagnetic and the Hg^{2+} is also diamagnetic. From the X-ray powder patterns Blinn *et al.* [1] concluded that the $HgCl_4{}^{2-}$ anion did not occur and the complex, also indicated as $[Ni(aet)_2HgCl_2]_n$, could not be formulated as $[Hg(Ni(aet)_2)_2]HgCl_4$.

We produced crystals with very similar electronic and magnetic properties, as the above-mentioned red species. However, our crystals were dark green. These crystals were suitable for X-ray single crystal diffraction. During the structure determination (in the stage of using Patterson methods) we came to the conclusion that the stoichiometry was not as expected. Based on elemental analysis data the formula should be $[Hg(Ni(aet)_3HgCl_2)_2](H_2O)_4$, in agreement with the X-ray structure. The present paper describes the results of the structure determination, as well as relevant spectroscopic and magnetic data.

Experimental

Synthesis and Crystal Growth

Starting materials

Bis(2-aminoethanethiol)nickel(II), $Ni(aet)_2$, was prepared by a standard procedure [2]. 2-Aminoethanethiolhydrochloride was commercially available (Aldrich), as was mercury chloride (Merck). These compounds were used without further purification.

Synthesis

A hot solution (60 °C) of 0.711 mmol (193.2 mg) mercury chloride in 12.5 ml water was added to a hot solution (60 °C) of 0.474 mmol (53.89 mg) 2-aminoethanethiolhydrochloride and 0.474 mmol (100 mg) $Ni(aet)_2$ in a 25 ml water and 12.5 ml ethanol mix.

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After a few days standing at room temperature beautiful green needles were formed, analysing as $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$ (calc. molecular weight 1389.4). *Anal.* Calc. (found): Ni: 8.45 (8.61), C: 10.36 (10.46), H: 3.17 (3.21), N: 6.05 (6.10), S: 13.84 (13.3), Hg: 43.31 (42.7), Cl: 10.21 (10.2)%. The compound was filtered, washed three times with ethanol and finally with diethyl ether and dried *in vacuo* (200 mm Hg) at about 45 °C. A flattened dark green crystal was selected for X-ray analysis and mounted on a diffractometer (Enraf-Nonius CAD-4); 4868 independent reflections were measured using the Ω-scan method. 2θ ranges from 2 to 30°.

Data Collection and Refinement

Data were collected at room temperature using Mo Kα radiation. No intensity profiles were measured. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Correction for absorption was applied according to a locally developed method [3] (maximum and minimum transmission factor 1.5066 and 0.1596 respectively). Only the observed reflections were used in the structure solution, non-observed reflections did not contribute to the refinement.

The structure was solved using Patterson and Fourier techniques and refined by least-squares methods. First isotropic and then anisotropic thermal parameters were used for all the non-hydrogen atoms. Sixteen hydrogen atoms were clearly localized from a difference synthesis and refined isotropically.

The function minimized during the refinement was $\Sigma w|\Delta F|^2$ (or $\Sigma w(|F_o| - |F_c|)^2$). Weighting schemes used in the last cycles were $w = 1/[\sigma^2(F_o) + 0.002F]$ with $\sigma(F_o)$ from counting statistics. The final R and R_w values were 0.035 and 0.040, respectively ($R = \Sigma|\Delta F|/|F_o|$ and $R_w = [(\Sigma w(\Delta F)^2)/(\Sigma w F_o{}^2)]^{1/2}$). Final difference maps were featureless.

Scattering factors used were taken from the literature tabulations [4]. All calculations were carried out on the Leiden University Amdahl 5086, using a set of locally developed programs.

The first attempt to determine a general position for mercury by using Patterson methods, was successful. A second mercury is present on a special position (multiplicity 4): a two-fold axis.

Fourier techniques showed the position of the nickel atom and later on the ligands forming the octahedron around nickel. Sixteen hydrogen atoms could be determined in that stage. The last two hydrogen atoms had to be calculated. The hydrogen atoms were kept at a fixed distance from their parent atom, using a riding motion on their parent atoms.

Crystal data and refinement parameters are listed in Table 1.

TABLE 1. Experimental data for the X-ray diffraction study on tetrachlorotrimercury(II)bis[tris(2-aminoethanethiolato)niccolate(II)] $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$

Crystal system	monoclinic
Molecular weight	1389.4
Space group	$C2/n$
a (Å)	20.076(5)
b (Å)	8.513(3)
c (Å)	19.654(5)
α (°)	90
β (°)	93.73(2)
γ (°)	90
V (Å^3)	3352(2)
Z	4
F(000)	2537.54
D_{calc} (g cm^{-3})	2.61
Molecular weight	1317.8469
Linear absorption (cm^{-1})	154.98
Diffractometer	Enraf-Nonius CAD-4
Scan type	ω
Max. scan time per reflection	60 s
Radiation	Mo Kα (λ = 0.710730)
2θ range (°)	2–30
h, k, l range	$-28 \leq h \leq 28; 0 \leq k \leq 12; -27 \leq l \leq 27$
Standard reflections	3 measured after every 5400 s
Unique total data	9733
No. independent reflections	4868
Unique observed data ($I \geq 2\sigma(I)$)	2983
No. variables	241
R	0.0349
R_w	0.0400

TABLE 2. Atomic fractional coordinates of $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$ (×10^5 for Ni and Hg; ×10^4 for S, Cl, C, O, N)

Atom	x/a	y/b	z/c	B_{iso} [a]
Ni	12933(2)	−37791(0)	12628(0)	147(2)
Hg1	18409(2)	4252(5)	−18886(2)	2289(9)
Hg2*	−25000	11351(7)	−25000	2405(14)
S11	1342(1)	−6028(3)	2012(1)	198(5)
S21	1373(1)	−1802(3)	2179(1)	190(5)
S31	2505(1)	−3823(3)	1104(1)	199(5)
N14	253(4)	−3898(9)	1387(3)	21(2)
N24	1198(4)	−1833(9)	613(3)	22(2)
N34	1235(4)	−5324(10)	436(3)	23(2)
C12	452(5)	−6159(12)	2131(4)	27(3)
C13	103(5)	−4599(12)	2051(4)	24(2)
C22	1121(5)	−178(11)	1627(5)	26(2)
C23	1407(6)	−342(12)	927(4)	27(2)
C32	2444(5)	−5005(11)	328(4)	25(2)
C33	1862(6)	−6149(12)	325(4)	29(3)
Cl(1)	715(1)	4742(4)	3957(1)	356(7)

(continued)

TABLE 2. *(continued)*

Atom	x/a	y/b	z/c	B_{iso}[a]
Cl(2)	2048(1)	1343(3)	3392(1)	291(6)
O1	169(4)	−7795(10)	199(4)	43(2)
O2	1043(4)	−3775(10)	−948(3)	41(2)

Estimated standard deviations in the least significant digits are given in parentheses. Special positions are marked with an asterisk.

[a] B_{iso} is defined as $8\pi^2/3\cdot\text{trace}(U)$ and are given as ×10 for C, N and O; ×100 for Ni, S and Cl; ×1000 for Hg.

Table 2 lists atomic coordinates and isotropic thermal parameters. See also 'Supplementary Material'.

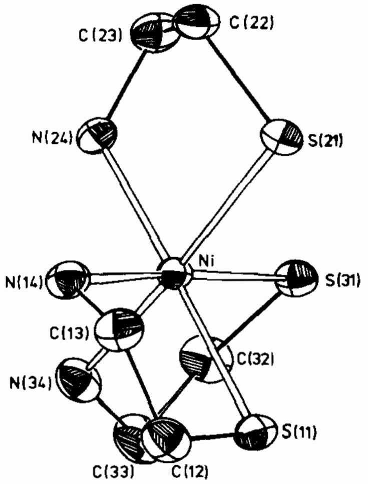

Fig. 1. ORTEP projection of the anionic species $[\text{Ni(aet)}_3]^-$.

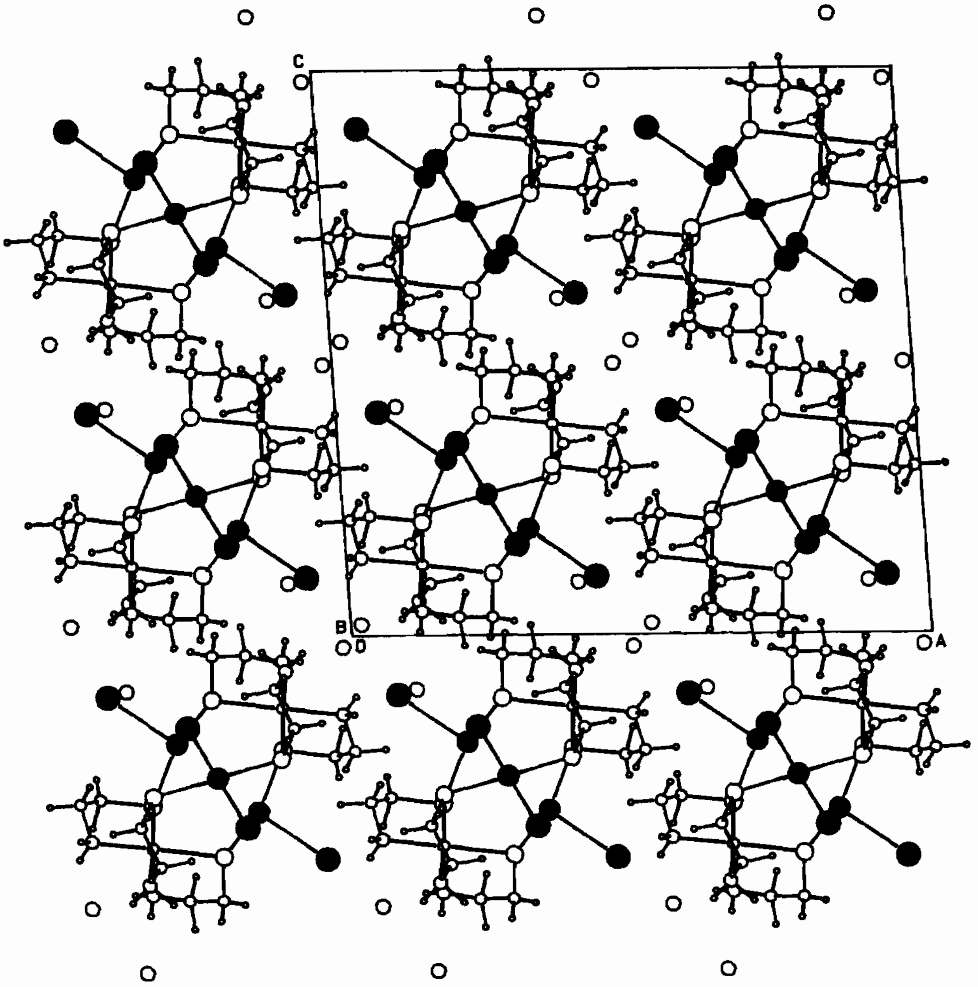

Fig. 2. Projection of the structure along the *b* axis, showing layers and unit cell. Larger filled circles are chlorine and smalle filled circles are mercury atoms. Largest open circles are sulfur atoms. Water molecules are only denoted with oxygen atoms.

Spectroscopy and Magnetism

Infrared spectra were recorded between 4000 and 250 cm^{-1} using a Perkin-Elmer Model 580B IR spectrophotometer. Samples were measured as KBr or CsCl pellets and as Nujol mulls between polyethene windows (<400 cm^{-1}). Ligand field spectra in the region 28 000–4000 cm^{-1} were recorded on a Perkin-Elmer 330 UV–Vis spectrophotometer using the diffuse-reflectance technique with MgO as a reference.

Magnetic susceptibility data were obtained on powdered samples in the temperature region 80–300 K on a Faraday balance. $CoHg(SCN)_4$ was used as a calibrant. The measurements were corrected for diamagnetism (with Pascal constants) and for temperature-independent paramagnetism.

Results and Discussion

General and Spectroscopy

The infrared spectrum of the title compound shows all the bands expected for the dehydronated aet ligand. No clear peaks were found that could be assigned to Hg–Cl and Hg–S bands in the far-infrared.

The ligand field maxima for the title compound are at 10 000 (sh), 11 000, 17 300 and about 28 500 cm^{-1}, in agreement with octahedral geometry for Ni^{2+} and a chromophore NiN_3S_3. Almost the same bands were reported earlier for the red product of Blinn *et al.* [1], and reproduced by us at 10 100 (sh), 11 000, 19 000 (sh on charge-transfer band). However, reproduction for the red product did not yield single crystals suitable for X-ray diffraction.

The magnetic susceptibility of the compound was obtained in the 300–86 K region and was found to decrease from 3.7 to 3.4 BM upon cooling. A plot of $1/\chi$ versus T produces a θ value of -35 K, indicative for an antiferromagnetic interaction. However, in the case of Ni(II) a contribution from a zero-field splitting might also be important.

Description of the X-ray Structure

The nickel(II) ions have a coordination number of six (as Blinn *et al.* [1] predicted). The geometry around nickel is almost perfectly octahedral, as would be expected for three equal chelating ligands. The $[Ni(aet)_3]^-$ unit and the numbering system are shown in Fig. 1. These octahedra are arranged in layers along the *bc* direction. In between the layers unusual cationic chloromercury species of formula $(Hg_3Cl_4)^{2+}$ act as bridging groups, using the S atoms of the aet ligand (see Fig. 2). One of the mercury atoms (Hg2) lies on a special position (a two-fold axis) between two anions of different asymmetric units (see Fig. 3). The Hg1 ion forms a bridge between anions in different asymmetric units (see Fig. 2). Along the *b* axis columns occur, as chloride ions build bridges between a Hg2 atom in one unit and two Hg1 atoms in a neighbouring unit. Water molecules fill the holes in the lattice, as shown in Fig. 2 (only the oxygen atoms are denoted).

In Table 3 bond lengths and distances are given. The Ni–N, Ni–S, Hg–Cl and Hg–S distances are in the range normally expected for similar compounds [5, 6]; angles are given in Table 4.

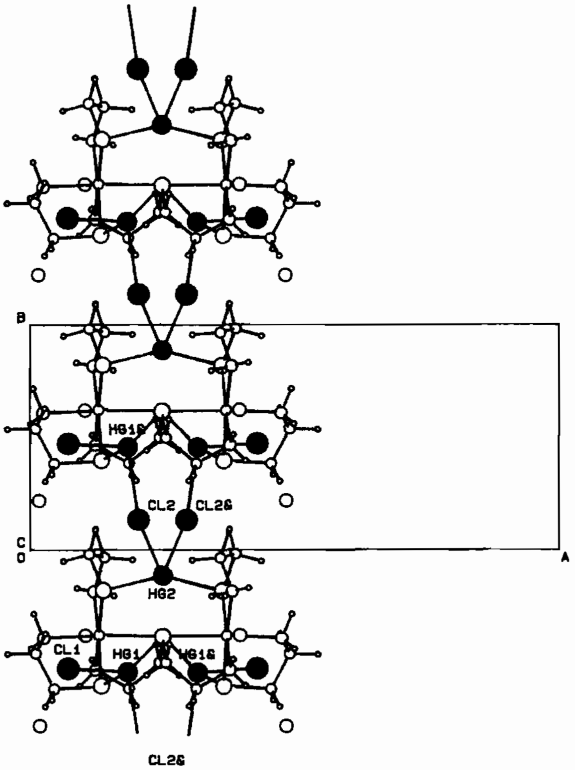

Fig. 3. Projection of the structure along the *c* axis, showing columns along *b*. For the meaning of the circles, see Fig. 2.

TABLE 3. Relevant interatomic distances of $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$

Ni–S11	2.413(2)
Ni–S21	2.462(2)
Ni–S31	2.473(3)
Ni–N14	2.120(8)
Ni–N24	2.093(7)
Ni–N34	2.088(7)
Hg1–S11^{4}	2.378(2)
Hg1–Cl(1)^{6}	2.895(3)
Hg1–Cl(2)^{6}	2.832(2)
Hg1–S31^{8}	2.388(2)
Hg2–S21^{1}	2.379(2)
Hg2–Cl(2)^{1}	2.924(2)
Hg2–S21^{3}	2.379(2)
Hg2–Cl(2)^{3}	2.924(2)

(continued)

TABLE 3. *(continued)*

S11–C12	1.82(1)
S21–C22	1.809(9)
S31–C32	1.825(9)
N14–C13	1.48(1)
N24–C23	1.46(1)
N34–C33	1.47(1)
C12–C13	1.51(1)
C22–C23	1.53(1)
C32–C33	1.52(1)

The superscript numbers following the text of atom 2 refer to the symmetry operators in the lattice, i.e. (1) = x, y, z; (2) = $x + \frac{1}{2}, y + \frac{1}{2}, z$; (3) = $-x + \frac{1}{2}, y, -z + \frac{1}{2}$; (4) = $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (5) = $x + \frac{1}{2}, -y, z + \frac{1}{2}$; (6) = $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (7) = $-x, -y, -z$; (8) = $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

TABLE 4. Relevant bond angles of $[Ni(aet)_3]_2Hg_3Cl_4(H_2O)_4$

Atoms	Angle (°)
S11–Ni–S21	95.63(8)
S11–Ni–S31	93.65(9)
S11–Ni–N14	83.9(2)
S11–Ni–N24	177.1(2)
S11–Ni–N34	88.5(2)
S21–Ni–S31	94.88(9)
S21–Ni–N14	88.1(2)
S21–Ni–N24	84.5(2)
S21–Ni–N34	175.8(2)
S31–Ni–N14	176.3(2)
S31–Ni–N24	89.2(2)
S31–Ni–N34	84.1(2)
N14–Ni–N24	93.2(3)
N14–Ni–N34	93.1(3)
N24–Ni–N34	91.5(3)
S11^4–Hg1–Cl(1)^6	103.54(8)
S11^4–Hg1–Cl(2)^6	90.87(7)
S11^4–Hg1–S31^8	153.09(8)
Cl(1)^6–Hg1–Cl(2)^6	92.67(8)
Cl(1)^6–Hg1–S31^8	91.04(8)
Cl(2)^6–Hg1–S31^8	111.20(8)
S21^1–Hg2–Cl(2)^1	90.26(8)
S21^1–Hg2–S21^3	152.4(1)
S21^1–Hg2–Cl(2)^3	109.86(8)
Cl(2)^1–Hg2–S21^3	109.86(8)
Cl(2)^2–Hg2–Cl(2)^3	87.7(1)
S21^3–Hg2–Cl(2)^3	90.26(8)
Ni–S11–C12	97.2(3)
Ni–S11–Hg1^5	112.4(1)
C12–S11–Hg1^5	104.8(3)
Ni–S21–C22	94.7(3)
Ni–S21–Hg2^2	111.9(1)
C22–S21–Hg2^2	101.6(4)
Ni–S31–C32	95.8(3)
Ni–S31–Hg1^8	115.54(9)
C32–S31–Hg1^8	103.2(3)
Ni–N14–C13	112.2(6)
Ni–N24–C23	114.7(5)
Ni–N34–C33	114.3(6)
S11–C12–C13	112.7(7)
N14–C13–C12	109.1(7)
S21–C22–C23	111.2(7)
N24–C23–C22	110.1(8)
S31–C32–C33	111.5(6)
N34–C33–C32	111.0(8)
Hg2^2–Cl(2)–Hg1^7	129.17(8)

The superscript numbers following the text of atoms refer to the symmetry operators (see Table 3).

Supplementary Material

Anisotropic thermal parameters, hydrogen parameters and listings of F_{obs} and F_{calc} are available from the authors.

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