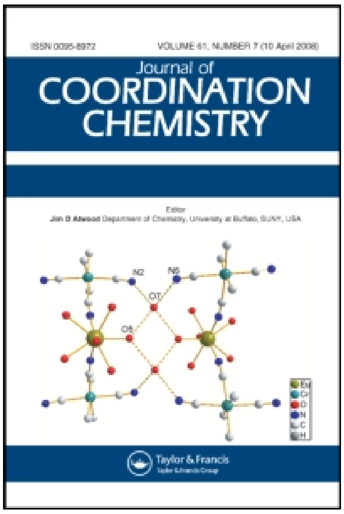

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COORDINATION COMPOUNDS OF NICKEL WITH TRITHIOCYANURIC ACID

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Nickel(II) complexes with a combination of trithiocyanuric acid and diamines or triamines of composition [Ni(aepa)(ttcH)(H_2O)], [Ni(dien)(ttcH)(H_2O)], [Ni(dpta)(ttcH)(H_2O)]·H_2O, [Ni(phen)$_2$(ttcH)]·H_2O, [Ni(phen)$_3$](ttcH)·5H_2O and [Ni(1,2-pn)$_3$](ttcH)·H_2O (aepa = *N*-(2-aminoethyl)-1,3-propanediamine, dien = diethylenetriamine, dpta = dipropylenetriamine, phen = 1,10-phenanthroline, 1,2-pn = 1,2-diaminopropane, ttcH$_3$ = trithiocyanuric acid) have been prepared. The compounds have been characterized by means of elemental analysis, IR and electronic spectroscopies and magnetochemical measurements. Selected complexes were studied by thermal analysis. The compounds can be characterized as distorted octahedral Ni(II) complexes. It was found that the trithiocyanuric dianion can act either as a bidentate ligand or be situated out of the coordination sphere of nickel. The crystal and molecular structure of [Ni(dpta)(ttcH)(H_2O)]·H_2O was determined. Crystals are monoclinic, space group $P2_1/n$, with $a = 20.316(4)$, $b = 7.967(2)$, $c = 21.401(4)$ Å, $\beta = 99.23(3)°$, $V = 3419.1(13)$ Å^3, $Z = 4$, $T = 293$ K. The nickel(II) atom is six-coordinated by three nitrogen atoms from dipropylenetriamine, nitrogen and sulphur from trithiocyanuric acid, and an oxygen atom from a water molecule in a distorted octahedral geometry.

Keywords: Nickel(II); trithiocyanuric acid; complexes; synthesis; X-ray structure

INTRODUCTION

The coordination chemistry of heterocyclic compounds is interesting not only for chemists but also because of its possible applications in industry,

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biology, pharmacology and analytical chemistry. Trithiocyanuric acid was used, for example, as a cross-linking agent for synthetic rubbers, in electroplating baths and in developing processes.[1-3] Inhibition activity for some enzymes was evaluated.[4,5] Formation of a Cu^{2+} complex with trithiocyanuric acid was used for spectrophotometric determination of copper.[6,7] The acid is a very promising ligand for its three N, S donor set. Polynuclear or mononuclear Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+} and Pb^{2+} complexes and their stoichiometry in solution were reported by Beezer and Chudy.[1] Resistivities and IR measurements of polynuclear complexes of Cu, Cd, Hg, Pb and Ag with trithiocyanuric acid have been reported.[8] Corbin *et al.*[9-11] reported a cyclopentadienyl trinuclear Ti(III) complex bridged by the trianion of trithiocyanuric acid. All of the complexes above were formed as insoluble precipitates and so their structural properties were not elucidated. Not many molecular structures involving trithiocyanuric acid in complexes have been solved to date as follows from the Cambridge Structural Database.[12] $[\{Os_3H(CO)_{10}\}_3(ttc)]$ was prepared by Ainscough *et al.*[13] and its structure established by a single-crystal X-ray analysis. Chan Chi-Keung *et al.*[14] have prepared, by the reaction of $ttcH_3$ with $CuCl(PPh_3)_3$ (PPh_3 = triphenylphosphine), a complex of composition $[\{Cu(PPh_3)\}_6(ttc)_2]$, where Cu(I) atoms are coordinated through N and S atoms from two virtually parallel triazine rings and the P atom of triphenylphosphine. The binuclear complex $[\{Co(en)_2\}_2(ttc)](ClO_4)_3 \cdot 2H_2O$ (en = ethylendiamine was prepared and characterized (single-crystal X-ray study) by Yamanari *et al.*[15] In order to investigate the coordination possibilities of trithiocyanuric acid to nickel we decided to synthetize mixed ligand complexes with N donor ligands. Such complexes can be interesting as potential models for biological systems. The other aim was to prepare a single-crystal of a nickel trithiocyanuric complex to confirm results emerging from our physico-chemical studies.

EXPERIMENTAL

Materials

Trithiocyanuric acid trisodium salt nonahydrate and amines were supplied by Aldrich. $NiCl_2 \cdot 6H_2O$ and 1,10-phenanthroline were obtained from Lachema, these were of p. a. grade. $[Ni(phen)_2(H_2O)_2]Cl_2 \cdot 3H_2O$ and $[Ni(phen)_3]Cl_2 \cdot 6H_2O$ were prepared by a method previously described.[16]

Syntheses

Preparation of [Ni(aepa)(ttcH)(H_2O)] and [Ni(dien)(ttcH)(H_2O)]

A solution of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) in water (50 cm^3) was mixed with solutions of appropriate triamines (0.13 resp. 0.12 cm^3, 1.2 mmol). The blue solutions were boiled and after cooling a solution of $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) in water (10 cm^3) with 1 cm^3 of 0.1 M HCl was added dropwise. Formation of blue precipitates was observed. The blue precipitates were filtered off, washed with small amounts of cold water and dried in a vacuum desiccator over KOH.

Preparation of [Ni(dpta)(ttcH)(H_2O)] · H_2O

A solution of $NiCl_2 \cdot 6H_2O$ (0.47 g, 2 mmol) in 50 cm^3 of water was added to a water solution (20 cm^3) of $ttcNa_3 \cdot 9H_2O$ (0.81 g, 2 mmol) with 2 cm^3 of 0.1 M HCl with stirring. A green precipitate formed was dissolved during boiling. Its colour turned dark brown. After cooling, dpta (0.34 cm^3, 2.4 mmol) was added. The brown solution turned green. On standing for a week blue crystals suitable for a single-crystal X-ray analysis were collected on a frit, washed with cold water and dried in air.

Preparation of [Ni(phen)$_2$(ttcH)] · H_2O

$[Ni(phen)_2(H_2O)_2]Cl_2 \cdot 3H_2O$ (0.87 g, 1.5 mmol) was dissolved in EtOH (50 cm^3) and a water solution (10 cm^3) of $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) was added dropwise. The yellow product was washed with water and EtOH and dried *in vacuo*.

Preparation of [Ni(phen)$_3$](ttcH) · 5H_2O

$[Ni(phen)_3]Cl_2 \cdot 6H_2O$ (0.78 g, 1 mmol) was dissolved in water (50 cm^3) and a water solution (10 cm^3) of $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) was added. The pink precipitate immediately formed was filtered off, washed with cold water and dried in air.

Preparation of [Ni(1,2-pn)$_3$](ttcH) · H_2O

The complex was prepared by reaction of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) with 1,2-pn (0.3 cm^3, 3.5 mmol) in 25 cm^3 of water and a water solution (10 cm^3) of $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) with 1 cm^3 of 0.1 M HCl.

The solution was allowed to stand for a week and the violet plates formed were collected and treated as above.

Physical Measurements

C, H, N, S analyses were performed on an EA 1108 instrument (Fisons). IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena) spectrophotometer; electronic spectra were recorded on a Specord M 40 (Carl Zeiss, Jena) instrument with samples in Nujol mulls. Magnetochemical measurements were performed at 296 K using the Faraday method on a magnetic device constructed by Z. Šindelář. $Hg[Co(SCN)_4]$ was used as calibrant. The correction for diamagnetism was calculated using Pascal's constants. Thermal decomposition was studied with a Q 1500 D Derivatograph (MOM Budapest) with a sample weight of 100–140 mg and temperature increase of 2.5° C min^{-1}.

X-ray Crystallography

A complete data set was collected on a Kuma KM-4 four-circle diffractometer with κ-axis using monochromatic Mokα ($u = 0.71073$ Å) radiation at 293(2) K. Unit-cell dimensions were calculated by least-squares refinement from 38 centred reflections within the $15.4° < 2\theta < 20.6°$ region. Diffraction intensities were measured by the ω–2θ scan technique in the interval $2.5° < 2\theta < 50.2°$. The intensities of two standard reflections (2 0 0, 1 1 1) were monitored after every 300 measurement over the duration of the experiment; no significant changes in intensities were detected. Data were corrected for absorption effects by the Walker and Stuart procedure.[17] A correction for extinction was not applied. The structure was solved by the heavy-atom method (SHELXS-86)[18] and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-93);[19] weighting scheme: $w = 1/[\sigma^2(F_o)^2 + (0.0572P)^2 + 11.4846P]$, where $P = (F_o^2 + 2F_c^2)/3$. The hydrogen atoms positions were found from differential Fourier maps, except for hydrogens belonging to the non-coordinated water molecules which were not localized. All their parameters were refined isotropically. All structure determination calculations were carried out on a PC-AT Pentium. Crystal data and structure refinement details for $[Ni(dpta)(ttcH)(H_2O)]\cdot H_2O$ are summarized in Table I. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table II.

TABLE I Crystal data and structure refinement details for [Ni(dpta)(ttcH)(H_2O)] · H_2O

Empirical formula	$C_{18}H_{44}N_{12}Ni_2O_4S_6$
Formula weight	802.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 20.316(4)$ Å $b = 7.967(2)$ Å $\beta = 99.23(3)°$ $c = 21.401(4)$ Å
Volume	3419.1(13) $Å^3$
Z	4
Density (calcd.)	1.559 $Mg\,m^{-3}$
Absorption coefficient	1.513 mm^{-1}
$F(000)$	1680
Crystal size	1.00 × 0.15 × 0.15 mm
Index ranges	$0 \leq h \leq 24, 0 \leq k \leq 9, -24 \leq l \leq 25$
Reflections collected	6211
Independent reflections	6030 [$R(int) = 0.0468$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6030/0/539
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R = 0.048, R_w = 0.124$
R indices (all data)	$R = 0.114, R_w = 0.153$
Largest diff. peak and hole	0.449 and −0.492 e $Å^{-3}$

RESULTS AND DISCUSSION

Analytical data are given in Table III. The magnetic moments of the Ni(II) complexes (see Table III) vary in the range 3.02–3.17 B.M. The values are typical of octahedrally coordinated Ni(II). The assumption is also supported by the electronic absorption spectra (see Table III). All the spectra are very similar. One set of *d–d* bands is observed at 17 000–20 000 cm^{-1} and can be attributed to [$^3A_{2g}$–$^3T_{1g}(F)$] transitions; the second at 29 000–30 000 cm^{-1} are to [$^3A_{2g}$–$^3T_{1g}(P)$] transitions.[20] The bands of the third transitions [$^3A_{2g}$–$^3T_{2g}$] were not observed in the range studied. Other bands can be assigned to CT or π–π^* transitions.

When we compare the IR spectrum[21] of $ttcH_3$ with spectra of the complexes we notice that a strong peak at 456 cm^{-1} together with a weak peak at 476 cm^{-1} of the free acid is shifted to 468 and 492 cm^{-1} for [Ni(dpta)(ttcH)(H_2O)] · H_2O; in spectra of [Ni(phen)$_3$](ttcH) · 5H_2O and [Ni(1,2-pn)$_3$](ttcH) · H_2O only one peak at 468 and 480 cm^{-1}, respectively, was found in the same region. No peaks were observed in the spectra of the other complexes. A peak at 722 cm^{-1} for the free acid was found in IR spectra of the complexes in the range 724–750 cm^{-1}. A strong broad peak at 1116 cm^{-1} of

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Ni(dpta)(ttcH)(H_2O)] \cdot H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni(1)	1415(1)	881(1)	1634(1)	36(1)
O(1)	938(3)	2656(7)	2149(2)	53(1)
O(2)	4645(4)	−340(12)	1604(5)	136(3)
S(1)	2542(1)	600(2)	2370(1)	46(1)
S(2)	3833(1)	−4088(2)	1294(1)	52(1)
S(3)	1573(1)	−1699(2)	110(1)	44(1)
N(1)	2102(3)	−734(6)	1283(2)	36(1)
N(2)	3172(2)	−1694(6)	1790(2)	38(1)
N(3)	2670(2)	−2785(6)	825(2)	36(1)
N(4)	1814(3)	2929(7)	1227(3)	45(1)
N(5)	590(3)	672(7)	909(3)	40(1)
N(6)	1119(4)	−1063(9)	2185(3)	57(2)
C(1)	2619(3)	−729(7)	1766(3)	36(1)
C(2)	3186(3)	−2777(7)	1309(3)	36(1)
C(3)	2136(3)	−1727(7)	784(3)	34(1)
C(4)	1351(4)	4113(9)	866(4)	54(2)
C(5)	885(4)	3253(11)	345(4)	56(2)
C(6)	349(4)	2252(10)	577(4)	53(2)
C(7)	18(4)	−275(10)	1062(4)	55(2)
C(8)	187(5)	−1949(10)	1366(5)	67(2)
C(9)	462(5)	−1885(14)	2054(5)	77(3)
Ni(2)	6700(1)	−1522(1)	1469(1)	33(1)
O(3)	6026(3)	186(6)	1769(2)	45(1)
O(4)	6395(7)	−1900(14)	−1294(6)	206(6)
N(7)	7508(2)	−3065(6)	1300(2)	32(1)
N(8)	8228(3)	−5010(7)	991(3)	42(1)
N(9)	8441(2)	−4069(6)	2025(2)	37(1)
N(10)	7206(3)	544(7)	1188(3)	48(1)
N(11)	6087(3)	−1764(7)	595(3)	43(1)
N(12)	6261(4)	−3490(9)	1907(4)	46(2)
S(4)	7641(1)	−1791(2)	2423(1)	40(1)
S(6)	7277(1)	−3934(2)	87(1)	48(1)
S(5)	9204(1)	−6535(3)	1716(1)	68(1)
C(10)	7901(3)	−3089(7)	1879(3)	34(1)
C(11)	8595(3)	−5119(8)	1586(3)	40(2)
C(12)	7687(3)	−3990(7)	836(3)	33(1)
C(13)	6828(5)	1732(9)	753(4)	60(2)
C(14)	6474(4)	906(12)	161(4)	61(2)
C(15)	5892(4)	−196(10)	251(4)	52(2)
C(16)	5488(4)	−2840(11)	575(4)	57(2)
C(17)	5631(5)	−4501(11)	903(5)	71(3)
C(18)	5679(4)	−4411(12)	1611(5)	64(2)

the free acid is, in the IR spectra of the complexes, split into 2–4 peaks observed in the 1000–1150 cm^{-1} region. New peaks are observed in spectra of the complexes in the range 1150–1270 cm^{-1}.

Thermal decomposition of $[Ni(dpta)(ttcH)(H_2O)] \cdot H_2O$ begins at 40°C with a loss of a non-coordinated water molecule ($\Delta m = 4.7\%$ [calcd. 4.5%]).

TABLE III Analytical data, electronic spectroscopic details and magnetic moments

Compound	*Found(Calcd.)* (%)				μ_{eff}	*Electronic spectra maxima*
	C	H	N	S	(*B.M.*)	$\times 10^3\,(cm^{-1})$
$[Ni(aepa)(ttcH)(H_2O)]$	26.8 (26.0)	5.1 (4.9)	22.9 (22.8)	25.5 (26.1)	3.13	17.5, 30.0 34.0
$[Ni(dien)(ttcH)(H_2O)]$	23.8 (23.7)	4.6 (4.5)	23.3 (23.7)	26.5 (27.1)	3.17	17.0, 30.0
$[Ni(dpta)(ttcH)(H_2O)]\cdot H_2O$	26.3 (26.9)	5.6 (5.5)	20.6 (21.0)	23.3 (24.0)	3.16	17.0, 29.0 34.5
$[Ni(phen)_2(ttcH)]\cdot H_2O$	53.2 (53.0)	3.4 (3.1)	15.8 (16.0)	14.9 (15.7)	3.16	20.0, 29.0
$[Ni(phen)_3(ttcH)]\cdot 5H_2O$	53.9 (54.2)	4.1 (4.1)	14.2 (14.6)	10.6 (11.1)	3.02	18.5, 29.0 35.0
$[Ni(1,2\text{-}pn)_3](ttcH)\cdot H_2O$	30.4 (30.4)	7.3 (7.0)	26.3 (26.6)	19.3 (20.3)	3.09	18.5, 30.0 35.0

Further spontaneous decomposition with a strong exothermic peak on the DTA curve is observed at 150°C. No weight loss corresponding to a loss of the second water molecule was found. A plateau observed on the TGA curve in the range 500–640°C is on the basis of calculation probably connected with formation of $NiSO_4$ as an intermediate of thermal decomposition. NiS was found as a final product (900°C) (%Ni: calcd. 14.6; found: 15.3). The $[Ni(phen)_2(ttcH)]\cdot H_2O$ complex starts to decompose at 50°C and is connected with dehydration of the complex ($\Delta m = 2.3\%$ [calcd. 2.8%]). The anhydrous product is thermally stable to 210°C. Further decomposition passes without formation of thermally stable intermediates and finishes at 860°C. The final product is NiO (%Ni: calcd. 9.6; found: 9.7). Five water molecules are lost at 60°C in the decomposition of $[Ni(phen)_3](ttcH)\cdot 5H_2O$ ($\Delta m = 10.8\%$ [calcd. 10.4%]). The anhydrous sample is stable to 190°C. A plateau between 310–370°C is observed on the TGA curve. Further decomposition is accompanied by a strong *exo*-effect on DTA curve. The final product (900°C) is also NiO (%Ni: calcd. 6.8; found: 6.6). From thermal analyses, it can be assumed that the water molecules are non-coordinated in $[Ni(phen)_2(ttcH)]\cdot H_2O$ and $[Ni(phen)_3](ttcH)\cdot 5H_2O$. On the basis of data we have obtained the complexes can be divided into two groups. To the first group belong complexes, which contain trithiocyanuric dianion coordinated to nickel atom as a bidentate N, S-donor ligand. The second group constitutes the complexes with a trithiocyanuric dianion situated out of the coordination sphere of the central atom.

The coordination mode of the trithiocyanuric dianion to the nickel atom was confirmed by a single-crystal X-ray analysis of [Ni(dpta)(ttcH)(H_2O)]·H_2O. The structure consists of two crystallographically independent molecules. The molecular structure of the complex studied is shown in Figure 1, while the crystal packing is drawn in Figure 2. Selected bond lengths and angles are given in Table IV. The central nickel(II) ion is

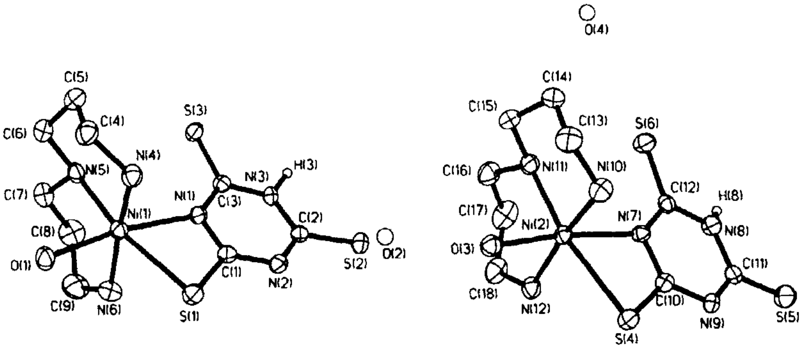

FIGURE 1 Molecular structure of the complexes (crystallographically independent molecules. Most H atoms are omitted for clarity.

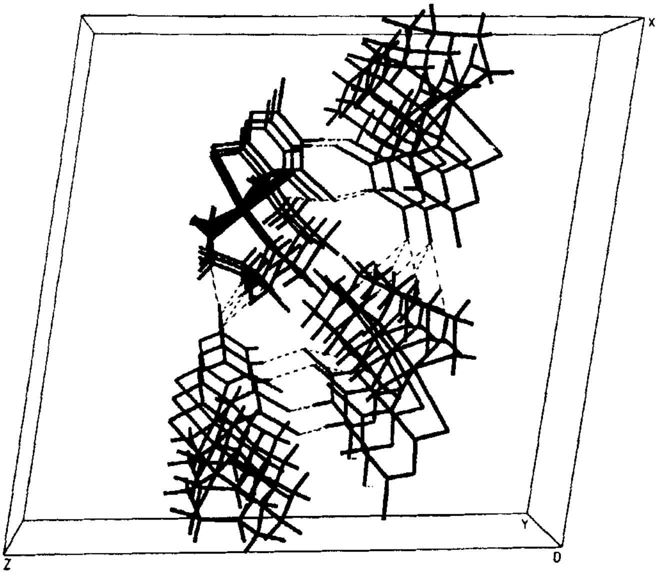

FIGURE 2 Crystal packing of the complex.

TABLE IV Selected bond lengths [Å] and angles [°] for [Ni(dpta)(ttcH)(H_2O)]·H_2O

Ni(1)–N(4)	2.075(6)	Ni(2)–N(10)	2.081(6)
Ni(1)–N(6)	2.093(7)	Ni(2)–N(11)	2.084(5)
Ni(1)–N(5)	2.100(5)	Ni(2)–N(12)	2.097(7)
Ni(1)–O(1)	2.120(5)	Ni(2)–O(3)	2.102(5)
Ni(1)–N(1)	2.122(5)	Ni(2)–N(7)	2.129(5)
Ni(1)–S(1)	2.572(2)	Ni(2)–S(4)	2.573(2)
Ni(1)–S(3)	3.913(2)	Ni(2)–S(6)	3.864(2)
S(1)–C(1)	1.697(6)	N(7)–C(12)	1.332(7)
S(2)–C(2)	1.683(6)	N(7)–C(10)	1.362(7)
S(3)–C(3)	1.692(6)	N(8)–C(12)	1.364(8)
N(1)–C(3)	1.341(7)	N(8)–C(11)	1.372(8)
N(1)–C(1)	1.350(8)	N(9)–C(11)	1.333(8)
N(2)–C(2)	1.347(8)	N(9)–C(10)	1.343(7)
N(2)–C(1)	1.355(8)	S(4)–C(10)	1.702(6)
N(3)–C(2)	1.351(8)	S(6)–C(12)	1.684(6)
N(3)–C(3)	1.365(7)	S(5)–C(11)	1.664(6)
N(4)–Ni(1)–N(6)	170.3(3)	N(10)–Ni(2)–N(12)	170.4(3)
O(1)–Ni(1)–N(1)	165.9(2)	O(3)–Ni(2)–N(7)	169.7(2)
N(5)–Ni(1)–S(1)	166.4(2)	N(11)–Ni(2)–S(4)	165.0(2)
C(1)–S(1)–Ni(1)	76.7(2)	C(12)–N(7)–C(10)	118.7(5)
C(3)–S(3)–Ni(1)	55.3(2)	C(12)–N(7)–Ni(2)	139.1(4)
C(3)–N(1)–C(1)	118.5(5)	C(10)–N(7)–Ni(2)	102.0(4)
C(3)–N(1)–Ni(1)	139.6(4)	C(12)–N(8)–C(11)	124.1(6)
C(1)–N(1)–Ni(1)	101.7(4)	C(11)–N(9)–C(10)	118.5(5)
C(2)–N(2)–C(1)	117.0(5)	C(13)–N(10)–Ni(2)	117.6(5)
C(2)–N(3)–C(3)	123.9(5)	C(15)–N(11)–C(16)	108.8(6)
C(4)–N(4)–Ni(1)	117.9(5)	C(15)–N(11)–Ni(2)	116.4(5)
C(7)–N(5)–C(6)	109.2(5)	C(16)–N(11)–Ni(2)	116.7(5)
C(7)–N(5)–Ni(1)	116.3(5)	C(18)–N(12)–Ni(2)	124.0(6)
C(6)–N(5)–Ni(1)	116.6(4)	C(10)–S(4)–Ni(2)	77.3(2)
C(9)–N(6)–Ni(1)	123.7(6)	C(12)–S(6)–Ni(2)	56.6(2)
N(1)–C(1)–N(2)	124.5(5)	N(9)–C(10)–N(7)	123.9(5)
N(1)–C(1)–S(1)	115.4(5)	N(9)–C(10)–S(4)	121.7(5)
N(2)–C(1)–S(1)	120.1(5)	N(7)–C(10)–S(4)	114.4(4)
N(2)–C(2)–N(3)	118.7(5)	N(9)–C(11)–N(8)	117.4(6)
N(2)–C(2)–S(2)	121.7(5)	N(9)–C(11)–S(5)	124.0(5)
N(3)–C(2)–S(2)	119.7(5)	N(8)–C(11)–S(5)	118.5(5)
N(1)–C(3)–N(3)	117.1(5)	N(7)–C(12)–N(8)	117.0(5)
N(1)–C(3)–S(3)	123.9(5)	N(7)–C(12)–S(6)	122.8(4)
N(3)–C(3)–S(3)	119.0(5)	N(8)–C(12)–S(6)	120.2(5)

six-coordinated by one sulphur atom and nitrogen atom from $ttcH^{2-}$, three nitrogen atoms from dipropylenetriamine and one oxygen atom from a water molecule. Thus, the coordination polyhedron has a distorted octahedral geometry. This is obvious from different values of bond lengths and angles in the vicinity of the nickel atoms and from deviations of atoms from least-squares planes fitted through the donor atoms[22] as seen in Tables IV and V. While the Ni–N distances for both molecules are quite normal and vary from 2.075(6) to 2.129(5) Å, the Ni–S bond lengths are

TABLE V Weighted least-squares planes fitted through selected atoms. Values are presented in the following sequence: atoms defining plane, then deviations [Å] of atoms from plane with c.s.d's in parentheses

Plane 1:	Ni(1), O(1), S(1), N(1), N(5), Ni(1) −0.001(1), O(1) 0.048(6), S(1) −0.004(2), N(1) 0.047(5), N(5) −0.033(5)
Plane 2:	Ni(1), N(4), N(5), N(6), S(1), Ni(1) −0.016(1), N(4) −0.082(6), N(5) 0.436(5), N(1) 0.047(5), N(5) −0.033(5)
Plane 3:	Ni(1), N(1), N(4), O(1), N(6), Ni(1) −0.018(1), N(1) −0.021(5), N(4) −0.134(7), O(1) −0.265(6), N(6) −0.174(7)
Plane 4:	Ni(2), O(3), S(4), N(7), N(11), Ni(2) −0.002(1), O(3) 0.065(5), S(4) −0.003(2), N(7) 0.062(5), N(11) −0.034(6)
Plane 5:	Ni(2), N(10), N(11), N(12), S(4), Ni(2) −0.016(1), N(10) −0.079(6), N(11) 0.484(6), N(12) −0.120(7), S(4) 0.033(2)
Plane 6:	Ni(2), N(7), N(10), O(3), N(12), Ni(2) 0.014(1), N(7) −0.150(5), N(10) −0.133(7), O(3) −0.181(5), N(12) −0.182(7)

TABLE VI Selected hydrogen bonds [distances in (Å)] and angles [in (°)] in the crystal structure of $[Ni(dpta)(ttcH)(H_2O)] \cdot H_2O$

D^a–H ... A^b	D^a–H	H...A^b	D^a–A^b	∠ D^aHA^b
O(3)–H(3BB)...O(2) [x, y, z]	0.82(8)	2.07(8)	2.80(1)	148(8)
O(1)–H(1AA)...S(2) [$-x+0.5, y+0.5, -z+0.5$]	1.00(7)	2.98(7)	3.570(6)	118(5)
O(1)–H(1BB)...S(5) [$x-1, y+1, z$]	0.74(8)	2.86(8)	3.554(6)	159(8)

[a] D = donor atom; [b] A = acceptor atom.

nearly identical: 2.572(2) [Ni(1)–S(1)], and 2.573(2) Å [Ni(2)–S(4)], respectively. These bond lengths are somewhat longer than typical Ni–S bond distances which lie in the 2.20–2.52 Å interval. We also find intramolecular non-bonding contacts between the nickel atoms and, S(3) and S(6) equal to 3.913(2), and 3.864(2) Å, respectively. The structure is stabilized by a network of 44 possible hydrogen bonds,[22] the most important of which are listed in Table VI.

Supplementary Material

Lists of structure factors, all bond lengths and angles, atomic coordinates and equivalent isotropic displacement parameters of H-atoms and anisotropic displacement parameters are available from Zdeněk Trávniček upon request.

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References

[1] A.E. Beezer and J.C. Chudy, *Thermochimica Acta*, **6**, 231 (1973) and references therein.
[2] Y. Nakamura, M. Saito, K. Mori and K. Tamura, *Nippon Gomu Kyokaishi*, **53**, 294 (1980).
[3] E.S. Raper, *Coord. Chem. Rev.*, **61**, 115 (1985).
[4] M.H. Iltzsch and E.E. Klenk, *Biochem. Pharmacol.*, **46**, 1849 (1993).
[5] M.H. Iltzsch and K.O. Tankersley, *Biochem. Pharmacol.*, **48**, 781 (1994).
[6] H. Nishida, *Bunseki Kagaku*, **28**, 563 (1979).
[7] H. Nishida, *Bunseki Kagaku*, **30**, 412 (1981).
[8] J.C. Chudy and J.A.W. Dalziel, *J. Inorg. Nucl. Chem.*, **37**, 2459 (1975).
[9] D.R. Corbin, L.C. Francesconi, D.N. Hendrikson and G.D. Stucky, *Inorg. Chem.*, **18**, 3069 (1979).
[10] L.C. Francesconi, D.R. Corbin, D.N. Hendrikson and G.D. Stucky, *Inorg. Chem.*, **18**, 3074 (1979).
[11] D.R. Corbin, L.C. Francesconi, D.N. Hendrikson and G.D. Stucky, *Chem. Commun.*, **6**, 248 (1979).
[12] F. Allen and O. Kennard, 3D Search and Research Using the Cambridge Structural Database, *Chemical Design Automation News*, **8**, 1, 31 (1993).
[13] E.W. Ainscough, A.M. Brodie, R.K. Coll, A.J.A. Mair and J.M. Waters, *Inorg. Chim. Acta*, **214**, 21 (1993).
[14] C.K. Chan, K.K. Cheung and C.M. Che, *Chem. Commun.*, 227 (1996).
[15] K. Yamanari, Y. Kushi, M. Yamamoto, A. Fuyuhiro, S. Kaizaki, T. Kawamoto and Y. Kushi, *J. Chem. Soc., Dalton. Trans.*, 3715 (1993).
[16] Gmelins Handbuch der Anorganischen Chemie, Nickel, Part C, Vol. 1 (Verlag Chemie, GmbH Weinheim, 1968), p. 420.
[17] N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
[18] G.M. Sheldrick, SHELXS-86, *Acta Crystallogr.*, **A46**, 467 (1990).
[19] G.M. Sheldrick, SHELXL-93, *Program for crystal structure refinement* (University of Göttingen, Germany, 1993).
[20] A.B.P. Lever, Inorganic Electronic Spectroscopy (Elsevier, Amsterdam, 1968), p. 343.
[21] C.J. Pouchert, *The Aldrich Library of Infrared Spectra* (Edition III) (Aldrich Chemical Company, Wisconsin, 1981).
[22] M. Nardelli, PARST-95, *J. Appl. Cryst.*, **28**, 659 (1995).