Synthesis, Spectroscopy and Magnetism of Mixed-valence Ni(II)–Ni(III) Compounds with (Benz)imidazolethioether, Acetates and Dithiolates as Ligands. Crystal Structure of (Acetato)(1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane)nickel(II) Bis(toluene-3,4-dithiolato)niccolate(III)

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Abstract

A series of mixed-valence compounds of general formula Ni(OAc)(LLLL)Ni(tdt)$_2$, in which tdt stands for the toluene-3,4-dithiolate anion and LLLL is a tetradentate N_2S_2 donor with two (benz)imidazole groups and two thioether groups, has been prepared and characterized.

The compounds are formed by spontaneous oxidation of the starting Ni(II) products in air. Characterization with spectroscopic measurements indicates cations Ni(LLLL)(OAc)$^+$ with divalent octahedral Ni(II), and anions Ni(tdt)$_2^-$ with square planar Ni(III). The crystal structure of one of the compounds, i.e. with LLLL = 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexanen (abbreviated bbdh), has been determined. The title compound crystallizes in space group $P\bar{1}$, $Z = 2$, $a = 14.132(7)$, $b = 13.345(8)$, $c = 10.906(7)$, $\alpha = 115.59(4)$, $\beta = 91.58(5)$, $\gamma = 100.74(4)°$.

The structure has been determined using conventional heavy atom methods, final $R_w = 0.057$ (including hydrogens) based on 3379 significant ($I > 2\sigma(I)$) reflections. Two anions Ni(tdt)$_2^-$, with Ni–S distances of 2.140(2)–2.153(2) Å, lie on centers of symmetry. There are strong indications of disorder in one of the Ni anions.

The cation [Ni(OAc)(bbdh)]$^+$ is six-coordinated by two oxygens of acetate (2.108(4) and 2.137(4) Å), two nitrogens of the benzimidazoles (2.026(5) and 2.047(5) Å), and two sulfurs of the thioethers (2.415(2) and 2.416(2) Å).

Introduction

Coordination compounds of Ni(II) and Ni(III) with thiolate ligands have been the subject of several studies in the previous two decades [1–5]. More recently Ni–thioether compounds have become available as well [6–9].

Nickel is an essential trace element present in many hydrogenases [10]. Spectroscopic and biochemical evidence suggested the presence of Ni in conjunction with sulfur and imidazole ligands, leading to an investigation of the imidazole–thioether–thiolate–nickel system. In attempts to prepare a compound Ni(bbdh)(tdt)$^{n+}$ (tdt = toluene-3,4-dithiolate; bbdh = 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane; $n = 0, 2$) an unexpected ionic product, analysing as Ni$_2$(OAc)(bbdh)(tdt)$_2$ was obtained. Similar compounds could be prepared with 1,7-bis(benzimidazol-2-yl)-2,6-di-thiaheptane (bbdhp), 1,7-bis(5-methyl-imidazole-4-yl)-2,6-dithiaheptane (bidhp) and 1,6-bis(1-methylbenzimidazol-2-yl)-2,5-dithiahexane.

Spectroscopic and magnetic studies showed the presence of both Ni(II) and Ni(III) and an average magnetic moment of 2.4 BM per nickel atom. A single crystal study of a representative example was therefore undertaken to elucidate the structure of these compounds and to enable the interpretation of its spectroscopic and magnetic properties.

Experimental

Starting Materials and Ligand Synthesis

3,6-Dithiaoctanedioic acid was synthesized according to the literature method [11]. The synthesis of the ligands was performed as follows: 1,6-bis(benzimidazol-2-y)-2,5-dithiahexane (bbdh) [12], 1,7-bis(benzimidazol-2-yl)-2,6-dithiaheptane (bbdhp) [13], 1,7-bis(*N*-methylimidazol-2-yl)-2,6-dithiaheptane (bidhp) [14] were prepared by the reported methods. 1,6-Bis(*N*-methylbenzimidazol-2-yl)-2,5-dithiahexane (Mebbdh) was prepared according to the N-methylation procedure with KOH and methyl iodide in acetone as described by Kikugawa [15].

Powdered potassium hydroxide (0.910 g, 16.25 mmol) was added to a stirred suspension of bbdh

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(1.15 g, 3.25 mmol) in acetone (25 ml). After a few min methyl iodide (0.507 g, 3.58 mmol) was added to the reaction mixture. The stirring was continued for 30 min. The precipitated product was filtered, thoroughly washed with water (3 × 25 ml) and recrystallized from methanol. The white needles obtained (yield 1.25 g, 90%, melting point (m.p.) 205–206 °C) were identified as 1,6-bis(*N*-methylbenzimidazol-2-yl)-2,5-dithiahexane by ^{1}H NMR spectroscopy: 2.75 (s, 4H, CH_2), 3.70 (s, 6H, CH_3), 3.84 (s, 4H, CH_2), 7.08 (m, 4H, ArH), 7.61 (m, 4H, ArH).

Synthesis of Coordination Compounds

One mmol of ligand LLLL was dissolved in 50 ml of warm ethanol. An ethanolic solution (10 ml) of $Ni(CH_3COO)_2(H_2O)_4$ (0.496 g, 2 mmol) and 20 ml of a solution of toluene-3,4-dithiolate (2 mmol) in a mixture of ethanol and dichloromethane (1:1) were added; stirring was continued for 30 min. The resulting deep green solution was filtered and allowed to stand at –15 °C for 24 h. The solid compounds were separated by filtration, washed with a small amount of ethanol and diethyl ether.

Physical Methods

Infrared spectra (4000–180 cm^{-1}) were recorded on a Perkin-Elmer PE380 spectrophotometer equipped with a PE infrared data station, using KBr pellets. Solid-state electronic spectra (28 000–5000 cm^{-1}) were recorded on a Beckman DK-2A spectrophotometer fitted with a reflectance attachment, using MgO as a reference.

Electron spin resonance spectra of the powdered compounds were obtained with a Varian E-3 spectrophotometer at X-band frequencies at room temperature and at 77 K (liquid nitrogen). Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequence of 99.5 MHz, using Me_4Si as internal standard.

X-ray powder diffraction diagrams of the investigated compounds were obtained with a Guinier-De Wolff camera; single-crystal photographs were taken on a Weissenberg camera, both using Cu Kα radiation. Magnetic susceptibility measurements (80–300 K) were carried out with use of the Faraday method.

Elemental analyses were performed by Dr F. Pascher, Bonn, F.R.G.

Crystal Growth

The single crystal of (acetato)(1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane)nickel(II) bis(toluene-3,4-dithiolato)niccolate(III) was obtained by recrystallization from a 1:1 mixture of absolute ethanol–dichloromethane). *Anal.* Calc. for $Ni_2C_{34}H_{33}S_6N_4O_2$: Ni, 13.99; C, 48.65; H, 3.96; N, 6.67; S, 22.92. Found: Ni, 14.01; C, 48.13; N, 6.73; S, 22.04%.

Data Collection and Refinement

A crystal of dimensions 0.6 × 0.2 × 0.1 mm was mounted on the diffractometer. Relevant crystallographic information is given in Table 1. Cell parameters were obtained from 24 reflections. No correction for absorption was applied. The significant reflections only were used in the structure determination and refinement. The anionic Ni positions were obtained by inspecting the Patterson function (the centricity of the space group was not yet known at this stage). Most of the other atomic positions were found using the program AUTOFOUR of Kinneging and de Graaff [16]. After determination of the positions of the remaining carbon atoms and isotropic refinement in $P\bar{1}$ the agreement factor R_w was 0.12. At this stage unrealistically high thermal parameters of several atoms of one of the anions, considered in conjunction with chemically improbable values of various distances in the model of the structure, induced us to try to refine the model without the centre of symmetry.

However, attempts to refine the structure in $P1$ did not lead to satisfactory results. After constraining the geometry of the anions to sensible values the refinement was continued in $P\bar{1}$. Anisotropic refinement without hydrogens resulted in an R_w value of 0.072. Refinement with the hydrogen atoms placed at calculated positions at a distance of 0.98 Å, gave a final R_w of 0.0566 ($R = 0.0451$). The maximum and minimum densities in the final difference Fourier are 0.82 and –0.62 e/A3 respectively. Scattering

TABLE 1. Crystal and diffraction data of Ni(OAc)(bbdh)Ni(tdt)$_2$

Crystal system	monoclinic
Space group	$P\bar{1}$
a (Å)	14.132(7)
b (Å)	13.345(8)
c (Å)	10.906(7)
α (°)	115.59(4)
β (°)	91.58(5)
γ (°)	110.75(4)
V (Å^3)	1809(2)
Z	2
D_{calc}	1.55
Molecular weight	839.42
Diffractometer	Enraf-Nonius CAD-4
Scan type	ω/θ
Radiation	monochromated Mo Kα
h, k, l range	–16 16, –15 15, 0 12
Standard reflections	3 measured every 1.5 h of radiation time
Unique reflections	5650
Significant reflections ($I > 2\sigma I$)	3379
No. variables	4401
R	0.0451
R_w	0.0566
R(int)	0.037

TABLE 2. Fractional atomic coordinates (×10^4) and B_{iso} (×10) of Ni(OAc)(bbdh)Ni$(tdt)_2$ [a]

Atom	x/a	y/b	z/c	B_{iso}
Ni(1)	24920(7)	48167(7)	44797(9)	304(2)
S(3)	3010(1)	3034(1)	3534(2)	364(5)
S(6)	1571(1)	4286(1)	2310(2)	391(5)
C(1)	2857(4)	6491(5)	6731(7)	36(2)
C(2)	3135(6)	7533(7)	8057(8)	68(3)
O(1)	2291(3)	6475(3)	5809(5)	34(1)
O(2)	3187(3)	5622(4)	6507(5)	35(1)
N(17)	5220(4)	5301(4)	3297(5)	35(2)
N(19)	3738(4)	5385(4)	3877(5)	30(2)
N(27)	−359(4)	3369(4)	4510(6)	42(2)
N(29)	1214(4)	4087(4)	4897(5)	35(2)
C(16)	5164(4)	6419(6)	3715(6)	34(2)
C(11)	4236(4)	6476(5)	4080(6)	32(2)
C(12)	3926(5)	7485(6)	4536(7)	42(2)
C(13)	4615(6)	8428(6)	4601(8)	55(3)
C(14)	5523(6)	8349(7)	4235(8)	55(3)
C(15)	5835(5)	7367(7)	3794(7)	46(2)
C(18)	4370(4)	4731(5)	3409(6)	30(2)
C(10)	4159(4)	3488(5)	3045(6)	38(2)
C(4)	2229(5)	2320(5)	1927(7)	48(2)
C(5)	2052(5)	3080(6)	1271(7)	47(2)
C(20)	414(4)	3648(6)	2611(7)	44(2)
C(28)	439(4)	3699(5)	3994(7)	37(2)
C(26)	−93(5)	3549(6)	5820(8)	41(2)
C(21)	913(4)	4001(5)	6059(8)	37(2)
C(22)	1407(5)	4277(6)	7314(8)	47(2)
C(23)	892(6)	4110(7)	8290(8)	54(3)
C(24)	−114(6)	3657(7)	8006(10)	60(3)
C(25)	−607(6)	3373(6)	6775(9)	50(3)
Ni(2)	0	0	0	457(4)
S(38)	−141(1)	932(1)	−1155(2)	543(7)
S(39)	1121(1)	−718(1)	−1135(3)	554(7)
C(31)	1386(5)	663(7)	−4330(8)	61(3)
C(32)	786(5)	992(6)	−3324(7)	55(3)
C(33)	681(4)	565(5)	−2336(5)	51(2)
C(34)	1232(4)	−210(4)	−2351(5)	51(2)
C(35)	1867(5)	−538(7)	−3375(8)	67(3)
C(36)	1931(6)	−124(7)	−4329(9)	68(3)
C(37)	1481(6)	1106(8)	−5361(10)	74(3)
Ni(3)	5000	5000	0	483(4)
S(48)	4417(2)	3260(2)	−414(3)	682(8)
S(49)	6419(1)	4677(2)	−353(3)	702(9)
C(41)	6063(10)	901(10)	−1593(12)	103(6)**
C(42)	5288(8)	1418(6)	−1243(9)	95(5)**
C(43)	5382(4)	2596(6)	−873(8)	66(3)**
C(44)	6290(6)	3236(2)	−861(8)	730(4)
C(45)	7077(6)	2681(10)	−1257(11)	103(5)**
C(46)	6976(10)	1544(10)	−1602(14)	113(6)**
C(47)	6072(11)	−320(10)	−1839(13)	146(7)**

[a] e.s.d.s in the least significant digits are given in parentheses. The atoms marked ** show high thermal anisotropy; B_{iso} is defined as $8\pi^2/3 \times \mathrm{trace}(U)$; special positions are marked with an asterisk. Coordinates of Ni(1) are given × 10^5. B_{iso} of Ni and S atoms are given × 10^2.

factors were taken from the International Tables for X-ray Crystallography [17], corrections for anomalous dispersion effects were applied to account for Ni and S. The atomic coordinates of the non-hydrogen atoms and their B_{eq} values are given in Table 2. See also 'Supplementary Material'.

Results and Discussion

Descripton of the Molecular and Crystal Structure of (Acetato)(1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane)nickel(II) Bis(toluene-3,4-dithiolato)-niccolate(III)

The compound consists of cations Ni(OAc)-(bbdh)$^+$ and counter ions Ni$(tdt)_2^-$. These counter anions are located at symmetry centers and show some disorder. Species of this type with a variety of organic cations have been known for quite some time. The Ni–S distances in our compound are typical for Ni(III) thiolates [3–5]. The two Ni$(tdt)_2^-$ anions are centered at 0, 0, 0 and 0.5, 0.5, 0 with half the anion formula as the asymmetric unit. In Fig. 1 one of these anions is depicted. Selected bond distances and angles are listed in Tables 3 and 4. The cationic part is quite interesting and a projection is redrawn in Fig. 2.

As is usually the case for bis(benzimidazole)-bis(thioether)tetradentate ligands, the imidazoles are in mutual *trans* orientation, with the two S atoms at a quite short distance. The few other nickel compounds reported before with this type of ligand have Ni–S distances of 2.4 Å [9]. In the case of copper with this type of tetradentate ligand, Cu–S distances of 2.34 to 3.00 Å have been reported previously [18, 19].

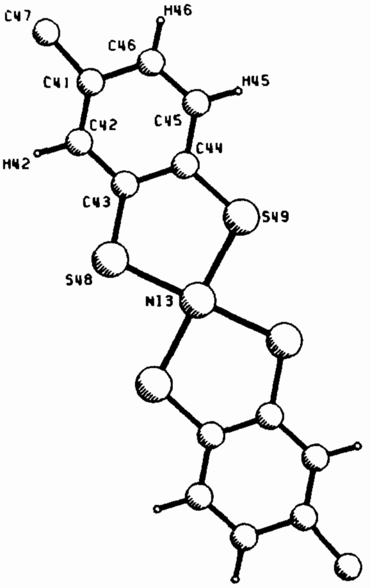

Fig. 1. Projection of one of the Ni$(tdt)_2^-$ anions.

TABLE 3. Bond lengths (Å) for Ni(OAc)(bbdh)Ni(tdt)$_2$

Ni(1)–O(1)	2.137(4)	C(13)–C(14)	1.37(1)
Ni(1)–O(2)	2.109(4)	C(14)–C(15)	1.35(1)
Ni(1)–N(19)	2.025(5)	C(18)–C(10)	1.495(8)
Ni(1)–N(29)	2.048(5)	C(4)–C(5)	1.523(9)
Ni(1)–S(3)	2.414(2)	C(20)–C(28)	1.48(1)
Ni(1)–S(6)	2.415(2)	C(26)–C(21)	1.412(9)
Ni(2)–S(38)	2.147(2)	C(26)–C(25)	1.37(1)
Ni(2)–S(39)	2.147(2)	C(21)–C(22)	1.377(9)
Ni(3)–S(48)	2.153(2)	C(22)–C(23)	1.38(1)
Ni(3)–S(49)	2.139(2)	C(23)–C(24)	1.41(1)
S(3)–C(10)	1.805(6)	C(24)–C(25)	1.35(1)
S(3)–C(4)	1.803(7)	S(38)–C(33)	1.732(1)
S(6)–C(5)	1.793(7)	S(39)–C(34)	1.731(1)
S(6)–C(20)	1.806(7)	C(31)–C(32)	1.374(2)
C(1)–C(2)	1.490(9)	C(31)–C(36)	1.415(1)
C(1)–O(1)	1.257(7)	C(31)–C(37)	1.48(1)
C(1)–O(2)	1.259(7)	C(32)–C(33)	1.420(2)
N(17)–C(16)	1.389(8)	C(33)–C(34)	1.4007(7)
N(17)–C(18)	1.347(7)	C(34)–C(35)	1.424(2)
N(19)–C(11)	1.413(7)	C(35)–C(36)	1.370(2)
N(19)–C(18)	1.323(7)	S(48)–C(43)	1.7311(5)
N(27)–C(28)	1.365(8)	S(49)–C(44)	1.7273(5)
N(27)–C(26)	1.381(9)	C(41)–C(42)	1.3798(8)
N(29)–C(28)	1.318(8)	C(41)–C(46)	1.414(1)
N(29)–C(21)	1.394(8)	C(41)–C(47)	1.52(1)
C(16)–C(11)	1.391(8)	C(42)–C(43)	1.4230(7)
C(16)–C(15)	1.403(9)	C(43)–C(44)	1.400(1)
C(11)–C(12)	1.384(8)	C(44)–C(45)	1.4252(8)
C(12)–C(13)	1.416(9)	C(45)–C(46)	1.374(1)

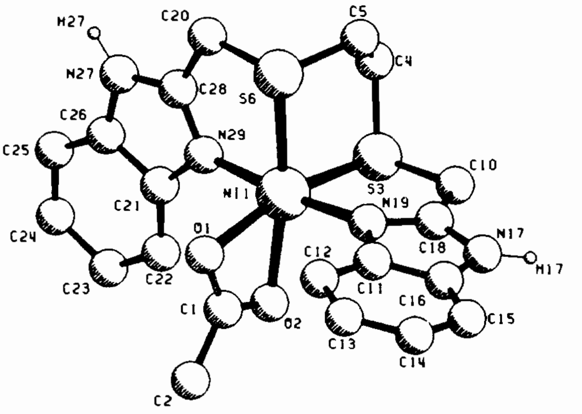

Fig. 2. Projection of the Ni(OAc)(bbdh)$^+$ cation. For clarity, most hydrogens have been omitted.

The acetato group binds chelating, didentate and in an almost symmetric manner to the nickel(II) ion. So far, we have not found chelating acetates containing this type of ligand. The Ni–O distances (Table 3) are normal for chelating acetates [20].

The cations and the anions are held in the lattice by van der Waals interactions, although some stacking between the benzimidazoles and the tdt ligands is also observed; typical distances are: 3.57 (C(18)–C(18))

TABLE 4. Bond angles in Ni(OAc)(bbdh)Ni(tdt)$_2$

O(1)–Ni(1)–O(2)	61.5(2)
O(1)–Ni(1)–N(19)	95.1(2)
O(1)–Ni(1)–N(29)	90.5(2)
O(2)–Ni(1)–N(19)	88.8(2)
O(2)–Ni(1)–N(29)	96.0(2)
S(3)–Ni(1)–S(6)	90.43(6)
S(3)–Ni(1)–O(1)	163.9(1)
S(3)–Ni(1)–O(2)	102.4(1)
S(3)–Ni(1)–N(10)	83.3(1)
S(3)–Ni(1)–N(29)	92.0(1)
S(6)–Ni(1)–O(1)	105.6(1)
S(6)–Ni(1)–O(2)	167.1(1)
S(6)–Ni(1)–N(19)	92.2(1)
S(6)–Ni(1)–N(29)	83.8(1)
N(19)–Ni(1)–N(29)	173.9(2)
S(38)–Ni(2)–S(39)	91.98(8)
S(48)–Ni(3)–S(39)	91.6(1)
S(48)–Ni(3)–S(48)[a]	179.90(3)
S(48)–Ni(3)–S(49)[a]	88.4(1)
S(49)–Ni(3)–S(48)[a]	88.4(1)
S(49)–Ni(3)–S(49)[a]	179.91(8)
S(48)[a]–Ni(3)–S(49)[a]	91.6(1)
C(10)–S(3)–C(4)	102.8(3)
C(5)–S(6)–C(20)	103.2(3)
C(2)–C(1)–O(1)	119.7(6)
C(2)–C(1)–O(2)	121.1(7)
O(1)–C(1)–O(2)	119.2(6)
Ni(1)–O(1)–C(1)	89.0(4)
Ni(1)–O(2)–C(1)	90.2(4)
C(16)–N(17)–C(18)	106.8(5)
Ni(1)–N(19)–C(11)	133.3(4)
Ni(1)–N(19)–C(18)	120.8(4)
C(11)–N(19)–C(18)	104.6(5)
C(28)–N(27)–C(26)	107.4(6)
Ni(1)–N(29)–C(28)	119.2(5)
Ni(1)–N(29)–C(21)	133.7(4)
C(28)–N(29)–C(21)	106.6(5)
N(17)–C(16)–C(11)	106.2(6)
N(17)–C(16)–C(15)	131.5(6)
C(11)–C(16)–C(15)	122.3(6)
N(19)–C(11)–C(16)	108.8(5)
N(19)–C(11)–C(12)	130.0(6)
C(16)–C(11)–C(12)	121.2(6)
C(11)–C(12)–C(13)	115.2(6)
C(12)–C(13)–C(14)	122.6(7)
C(13)–C(14)–C(15)	122.5(7)
C(16)–C(15)–C(14)	116.2(7)
N(17)–C(18)–N(19)	113.6(6)
N(17)–C(18)–C(10)	122.7(5)
N(19)–C(18)–C(10)	123.8(6)
S(3)–C(10)–C(18)	111.9(4)
S(3)–C(4)–C(5)	115.3(5)
S(6)–C(5)–C(4)	115.7(5)
S(6)–C(20)–C(28)	112.8(5)
N(27)–C(28)–N(29)	112.0(6)
N(27)–C(28)–C(20)	122.8(6)
N(29)–C(28)–C(20)	125.2(6)
N(27)–C(26)–C(21)	105.9(7)
N(27)–C(26)–C(25)	132.2(7)

(continued)

TABLE 4. *(continued)*

C(21)–C(26)–C(25)	122.0(8)
N(29)–C(21)–C(26)	108.2(7)
N(29)–C(21)–C(22)	132.1(6)
C(26)–C(21)–C(22)	119.7(7)
C(21)–C(22)–C(23)	118.5(7)
C(22)–C(23)–C(24)	120.3(8)
C(23)–C(24)–C(25)	121.6(8)
C(26)–C(25)–C(24)	117.9(7)
Ni(2)–S(38)–C(33)	104.9(2)
Ni(2)–S(39)–C(34)	104.7(2)
C(32)–C(31)–C(36)	116.7(8)
C(32)–C(31)–C(37)	122.8(7)
C(36)–C(31)–C(37)	120.5(7)
C(31)–C(32)–C(33)	123.2(6)
S(38)–C(33)–C(32)	121.9(4)
S(38)–C(33)–C(34)	118.9(4)
C(32)–C(33)–C(34)	119.1(4)
S(39)–C(34)–C(33)	119.3(4)
S(39)–C(34)–C(35)	122.8(5)
C(33)–C(34)–C(35)	117.9(4)
C(34)–C(35)–C(36)	121.2(7)
C(31)–C(36)–C(35)	121.9(8)
Ni(3)–S(48)–C(43)	104.7(3)
Ni(3)–S(49)–C(44)	105.5(3)
C(42)–C(41)–C(46)	120(1)
C(42)–C(41)–C(47)	126(1)
C(46)–C(41)–C(47)	114(1)
C(41)–C(42)–C(43)	121.6(9)
S(48)–C(43)–C(42)	122.0(7)
S(48)–C(43)–C(44)	119.4(6)
C(42)–C(43)–C(44)	118.6(5)
S(49)–C(44)–C(43)	118.6(6)
S(49)–C(44)–C(45)	122.3(7)
C(43)–C(44)–C(45)	119.0(6)
C(44)–C(45)–C(46)	122(1)
C(41)–C(46)–C(45)	119(1)

[a]Related by a center of symmetry.

and 3.52 (C(18)–C(12)) Å. Hydrogen bonds are present between the imidazole groups from one unit and acetate oxygen from nearby units, thereby forming chains in the lattice. The distances involved are N(27)...O(1) = 2.806(6) Å and N(17)...O(2) = 2.804(6) Å.

Spectroscopy and Magnetism

To better understand the structure of the compound, it was investigated whether the bbdh ligand could be replaced by related ligands with an N_2S_2 donor set. Indeed similar complexes could be obtained with Mebbdh (N-methylated bbdh), with the C_2H_4 bridge between the thioethers replaced by a C_3H_6 bridge (bbdhp) and with the benzimidazole group replaced by an imidazole group (bidhp).

Indeed all four ligands yielded compounds [Ni(OAc)(LLLL)] [Ni(tdt)$_2$]. The ligand-field spectra of the four compounds are all quite similar with band maxima at 7300–7500(w), 10700(s), 12000(sh), 14700(sh), 21700(m) and 27100(s) cm^{-1}. These band maxima are simple additions of the Ni(tdt)$_2^-$ chromophore with Ni(III) bands at 10700, 12000 and 21700 cm^{-1} and of distorted Ni(OAc)(LLLL)$^+$ with Ni(II) bands at 7400, 10700 (doublet due to low symmetry), 14700 and 27100 cm^{-1}. So, the anions consist of square-planar Ni(III) in the low-spin configuration, whereas the cation contains octahedrally-based Ni(OAc)(LLLL), with high-spin Ni(II) [21].

The infrared spectra of the compounds show the characteristic bands of Ni(tdt)$_2^-$ and, in addition, bands due to acetate (C–O at 1540 cm^{-1}) and the ligands. In case of the non-methylated ligands the N–H stretching vibrations are at 3200 cm^{-1} in agreement with the hydrogen bond pattern observed in the solid state.

The EPR spectra of the compounds show just a single band at $g = 2.21$ which is attributed to low-spin Ni(III) [10]. As expected the Ni(II) species does not show signals, because the zero-field splitting is apparently larger than the microwave frequency.

Powder-magnetic susceptibilities were recorded to check whether interaction between Ni(II) and Ni(III) would be present. The curve of χ versus T for Ni(bbdh)(OAc)Ni(tdt)$_2$, however, shows clear Curie behaviour, in agreement with the small stacking interactions. The overall magnetic moment of 2.4 BM can be understood from a simple addition of Ni(II) with a moment of 3.4 BM and diamagnetic Ni(III).

Conclusions

The results described above have made clear that mixed-valence species are easily formed under aerobic conditions, when a dithiolate ligand and a neutral ligand are reacted with Ni(II) acetate. The aim of preparing mononuclear species Ni(LLLL)(tdt)$^+$-(OAc)$^-$ cannot be realized, not even under anaerobic conditions. The resulting new species Ni(OAc)-(LLLL)$^+$ appears to be general, at least for the four ligands studied in this case.

Unfortunately, similar isomorphous Co(II) compounds could not be obtained.

Supplementary Material

Anisotropic temperature parameters and the hydrogen positions, as well as Tables of observed and calculated structure factors are available from the authors on request.

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