

Scientific paper

Bis(1,2-dithiosquarato)nickelates(II): Synthesis, Structure, EPR and Thermal Behavior

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Dedicated to the memory of Prof. Dr. Jurij V. Brenčič.

Abstract

1,2-Dithiosquaratonickelates are available by direct synthesis from metal salts with dipotassium-1,2-dithiosquarate and the appropriate counter cations. The synthesis and characterization, including mass spectrometry, of a series 1,2-dithiosquaratonickelates(II), $[\text{Ni}(\text{dtsq})_2]^{2-}$, with several „onium“ cations is reported and the X-ray structures of two diamagnetic complexes, $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ and $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ with sterically demanding counter ions are presented. The diamagnetic nickel complexes have been doped as host lattices with traces of Cu(II) to measure EPR for additional structural information. The thermal behavior of this series is studied by thermogravimetry and differential thermal analysis (TG/DTA). The thermolysis in air as well as under nitrogen atmosphere of these complexes results in nickel oxide nano-particles in all cases, which are characterized by X-ray powder diffraction.

Keywords: 1,2-Dithiosquarate, 1,2-Dithiosquaratonickelate, X-ray structure, TG/DTA, Nickel oxide, EPR spectroscopy

1. Introduction

1,2-Dithiolenes and 1,2-dithiolates belong to the best investigated classic ligand systems due to their interesting properties.^{1–6} During the last few years they have gained a renewed interest to study their transition metal complexes as building blocks *e.g.* for conducting or magnetic materials.^{7–12} Investigations about the thermal decomposition of these type of complexes, especially the thiosquaratometalates, and the resulting materials are relatively rare. Based on the classical thermal decomposition of metal oxalates for the preparation of metal oxides for different applications, we have investigated the thermal decomposition of 1,2-dithiosquaratonickelates. The zinc oxalate is one of the first thermally investigated oxalates and is still in the focus of interest today. A patent for the zinc oxide production, based on the thermal decomposition of the oxalate, and the subsequent usage as hydrogenation catalyst for the methanol production dates back to 1930.¹³ During the last years zinc oxalate was discussed as a precursor of nano-structured, large surface area ZnO particles^{14–18} with an enormous applicability in the field of catalysis, opto-electronics and electronics.^{19–31} Even the

related nickel(II) oxalate and the decomposition product NiO is in the center of attention since years.^{32–37} Micro- and nano-structured nickel oxides in form of spheres, particles or rods are reported.^{17,22,38–43} Porous nano-particles with diameters between 30 and 80 nm were generated by thermal decomposition of the oxalates at temperatures around 500 °C and were used in electronics for anode materials in lithium ion accumulators with high storage capacity.³⁸ In the presence of surfactants and NiC_2O_4 precursors the formation of NiO nano-rods at 900 °C is known.³⁹ Even at lower temperatures, *i.e.* 350–450 °C, the synthesis of interesting mesoporous structures from nickel(II) oxalates is reported.^{17,40} Nickel(II) oxides are established as multiple catalysts in the chemical industries, *e.g.* the catalytic effect for the carbon monoxide oxidation,^{44–45} for the degradation of N_2O ,⁴⁶ and for the dehydrogenation of aliphatic alcohols.⁴⁷ In this study we have synthesized a series of structurally related bis(1,2-dithiosquarato)nickelates(II) with different counter cations, namely „onium“ cations. 1,2-Dithiosquaratonickelates are available by direct synthesis from solutions of metal salts with dipotassium-1,2-dithiosquarate and the appropriate counter cations. The related, sulfur or selenium containing 1,2-

dichalcogenooxalates in form of bis(1,2-dichalcogenoxalato)metalates(II) precursors represent also an excellent basis for the thermally induced formation of different metal chalcogenides (metal oxides, metal sulfides, metal selenides). Next to the nickel oxide, all metal chalcogenides with their outstanding properties were used as starting materials for catalysts and different semiconductor devices.^{48–64} Compounds with two- or three-dimensional structures directed by different cations are promising precursors for the formation of micro- and/or nano-structured particles.

2. Experimental

2.1. Materials

Nickel(II) chloride hexahydrate (*p.a.*, Merck), the substituted ammonium and phosphonium bromides (Sigma Aldrich), acetonitrile, diisopropyl ether (*p.a.*, Merck) and ethanol (99%, Berkel AHK) were used as purchased without any further purification.

2.2. Syntheses

The ligand potassium 1,2-dithiosquarate (K_2dtsq) was synthesized following a modified method as described by Eggerding and West.⁶⁵ For the synthesis of the bis(1,2-dithiosquarato)nickelates(II) we followed in general the synthetic protocol of Wenzel *et al.*⁶⁶ To a solution of 59.4 mg (0.25 mmol) $NiCl_2 \cdot 6H_2O$ in 20 mL of water a solution of 111.2 mg (0.5 mmol) K_2dtsq in about 10 mL water is added. To the resulting brown solution 0.5 mmol of the appropriate cation salt dissolved in 15 mL water is slowly (in about 30 min) added and the solution is stirred for 1 h. The obtained light brown, micro crystalline products were filtered off, washed with 2-propanol and dried in vacuum. The yield of the complexes was nearly quantitative.

Bis(methyltriphenylphosphonium)bis(1,2-dithiosquarato)nickelate(II)

Cation salt: 178.6 mg (0.5 mmol) $MePh_3PBr$ in 15 mL H_2O . $C_{46}H_{36}N_2NiO_4S_4$ ($M = 901.68 \text{ g mol}^{-1}$). Yield: 183 mg, 82%. Mp.: 220 °C. Elemental analysis, measured (calc.): C 61.60 (61.27), H 4.13 (4.02), S 4.36 (4.23)%. IR (KBr): 3058, 2977, 2908 (w, ν_{C-H}), 1726, 1690, 1662 (s, ν_{C-O}), 1166 (m, ν_{C-C-S}), 903 (w, ν_{C-S}) cm^{-1} . MS (ESI⁻) *m/z* measured (calc.): 623.6 (623.9) [M-cat+H]⁻.

Bis(butyltriphenylphosphonium)bis(1,2-dithiosquarato)nickelate(II)

Cation salt: 199.7 mg (0.5 mmol) $BuPh_3PBr$ in 20 mL H_2O /ethanol (1:1). Single crystals for X-ray crystallography were grown from a solution of the complexes in acetonitrile layered with diisopropyl ether after several days (yellow crystals).

$C_{52}H_{48}N_2NiO_4S_4$ ($M = 985.84 \text{ g mol}^{-1}$). Yield: 196 mg, 80%. Mp.: 214 °C. Elemental analysis, measured (calc.): C 63.39 (63.35); H 4.76 (4.91), S 3.15 (13.05)%. IR (KBr): 3058, 2957, 2929 (w, ν_{C-H}), 1724, 1690 (s, ν_{C-O}), 1166 (m, ν_{C-C-S}), 914 (w, ν_{C-S}) cm^{-1} . MS (ESI⁻) *m/z* measured (calc.): 665.6 (666.0) [M-cat+H]⁻.

Bis(hexyltriphenylphosphonium)bis(1,2-dithiosquarato)nickelate(II)

Cation salt: 213.7 mg (0.5 mmol) $HexPh_3PBr$, in 20 mL H_2O /ethanol (1:1). Single crystals for X-ray crystallography were grown from a solution of the complexes in acetonitrile layered with diisopropyl ether after several days (yellow crystals).

$C_{56}H_{56}N_2NiO_4S_4$ ($M = 1041.94 \text{ g mol}^{-1}$). Yield: 215 mg, 83%. Mp.: 182–184 °C. Elemental analysis, measured (calc.): C 64.62 (64.55), H 5.36 (5.42), S 2.44 (12.31)%. IR (KBr): 3054, 3036, 2951, 2924, 2855 (w, ν_{C-H}), 1725, 1700 (s, ν_{C-O}), 1397 (m, ν_{C-C-O}), 1164 (m, ν_{C-C-S}), 910 (w, ν_{C-S}) cm^{-1} . MS (ESI⁻) *m/z* measured (calc.): 693.6 (693.0) [M-cat]⁻.

Bis(benzyltriethylammonium)bis(1,2-dithiosquarato)nickelate(II)

Cation salt: $BzEt_3NBr$, 136.1 mg (0.5 mmol) in 15 mL H_2O . $C_{34}H_{44}N_2NiO_4S_4$ ($M = 731.68 \text{ g mol}^{-1}$). Yield: 131 mg, 72%. Mp.: 158–160 °C. Elemental analysis, measured (calc.): C 55.97 (55.81); H 5.70 (6.06), N 4.07 (3.83), S 7.46 (17.53)%. IR (KBr): 3014, 2981 (w, ν_{C-H}), 1725, 1693 (s, ν_{C-O}), 1167 (m, ν_{C-C-S}), 913 (w, ν_{C-S}) cm^{-1} . MS (ESI⁻) *m/z* measured (calc.): 538.7 (539.0) [M-cat+H]⁻.

Bis(benzyltributylammonium)bis(1,2-dithiosquarato)nickelate(II)

Cation salt: $BzIBu_3NBr$ 178.2 mg (0.5 mmol) in 15 mL H_2O . $C_{46}H_{68}N_2NiO_4S_4$ ($M = 900.00 \text{ g mol}^{-1}$). Yield: 183 mg, 81%. Mp.: 167–168 °C. Elemental analysis, measured (calc.): C 61.47 (61.36); H 7.23 (7.61), N 8.26 (3.11), S 4.12 (14.25)%. IR (KBr): 2961, 2871 (w, ν_{C-H}), 1726, 1689 (s, ν_{C-O}), 1376 (m, ν_{C-C-O}), 1166 (m, ν_{C-C-S}), 913 (w, ν_{C-S}) cm^{-1} . MS (ESI⁻) *m/z* measured (calc.): 622.6 (623.1) [M-cat+H]⁻.

For the doping of the diamagnetic bis(1,2-dithiosquarato)nickelates with Cu(II) the same synthetic procedures have been performed but with 3–5% of Cu(II), as $CuCl_2$, in the starting Ni(II) salt solution.

2.3. Methods

All melting and decomposition points were determined on a Boetius hot stage microscope (Analytik Dresden). Elemental analyses for the elements C, H, N and S of the synthesized compounds were determined with an instrument from the company Elementaranalysen GmbH, Typ Vario EL III. Infrared spectra (IR) were measured between 4000 and 400 cm^{-1} on a Perkin-Elmer 16 PC FT-IR

as KBr discs. X-ray powder diffraction (XRD) patterns were recorded with 2θ between 3 and 70° on a Bruker AXS D5005 powder diffractometer on a silicon support. Materials were identified using the JCPDS database.⁶⁷ The calculated exact masses are according to isotopes highest natural abundance (monoisotopic mass).⁶⁸ Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed on a Linseis L81 thermo-balance in air or in a dynamic nitrogen atmosphere with 50 mL min^{-1} from 25 to $800 / 1000^\circ \text{C}$ at 10 K min^{-1} . Aluminum oxide crucibles were used as reference for DTA. EI-mass spectra were recorded on a SSQ 710 from Thermo Fisher Scientific at 70 eV using the direct inlet system. The compounds were injected as methanol solutions or dispersions (HPLC-grade). The calculation of the isotopic pattern was done with the software XCalibur.⁶⁹ ESI-mass spectra were obtained in positive and negative ion mode using an ESI-Q-TOF_{micro} quadrupole time-of-flight mass spectrometer (Waters Corporation). Solutions of the compounds in acetonitrile (HPLC-grade) were injected using an integrated syringe pump at a flow rate varying from 5–10 $\mu\text{L/min}$. The capillary voltage was set to 3.7 kV. Spectra calculations were performed with the Program MassLynxTM.⁷⁰ X-ray crystallography data were collected at 150 K on a STOE Imaging Plate Diffraction System IPDS-2 using graphite monochromatized Mo- K_α radiation with $\lambda = 0.71073 \text{ \AA}$. The measured

data were corrected by a spherical absorption correction as well as for Lorentz, polarization and extinction effects using the program X-Area.⁷¹ The structures were solved with SHELXS-97 using direct methods and refined against F^2 by means of full-matrix least-squares procedures with SHELXL-97.^{72–73} The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated in their expected positions and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C–H distances of 0.93 \AA for aromatic H atoms and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and distances of 0.96 \AA for methyl hydrogen atoms and 0.97 \AA for methylene hydrogen atoms. The programs DIAMOND and ORTEP were used for graphical presentation of the structures.^{74–75} Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by e-mail: deposit@ccdc.cam.ac.uk on quoting the deposition numbers CCDC-1033612 (for $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$) and -1033613 (for $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$).

3. Results and Discussion

3.1. X-ray Structures

The coordination compounds $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$, $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ were obtained as single crystals

Table 1. Crystallographic data and refinement parameters for $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ and $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$.

Compound	$(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$	$(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$
Formula	$\text{C}_{55}\text{H}_{48}\text{NiO}_4\text{P}_2\text{S}_4$	$\text{C}_{56}\text{H}_{56}\text{NiO}_4\text{P}_2\text{S}_4$
Molar mass / g mol^{-1}	985.79	1041.9
Crystal size / mm	$0.90 \times 0.21 \times 0.21$	$0.80 \times 0.59 \times 0.26$
Temperature / K	150	150
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
$a / \text{ \AA}$	8.9132(3)	9.2459(3)
$b / \text{ \AA}$	14.8200(4)	15.3790(5)
$c / \text{ \AA}$	17.7945(6)	18.2004(5)
$\alpha / ^\circ$	90	90
$\beta / ^\circ$	97.728(3)	102.553(2)
$\gamma / ^\circ$	90	90
$V / \text{ \AA}^3$	2329.2(1)	2526.1(1)
Z	2	2
Density (calculated) / $\text{g} \cdot \text{cm}^{-3}$	1.406	1.370
μ / mm^{-1}	0.711	0.659
$F(000)$	1028	1092
θ range / $^\circ$	1.79–25.0	1.75–25.0
Refl. measured	29769	32117
Refl. independent [R_{int}]	4109 [0.0445]	4438 [0.0263]
Refl. observed [$I > 2\sigma(I)$]	3744	4114
Parameters	287	305
R_1, wR_2	0.0238, 0.0560	0.0221, 0.0551
$R_1, wR_2 [I > 2\sigma(I)]$	0.0209, 0.0550	0.0203, 0.0544
Goodness of fit	1.043	1.068
Max. diff. peak/hole / $\text{e} \cdot \text{ \AA}^{-3}$	0.292/–0.220	0.283/–0.228

suitable for X-ray structure determination. Table 1 summarizes the crystallographic data and refinement parameters for the two complexes.

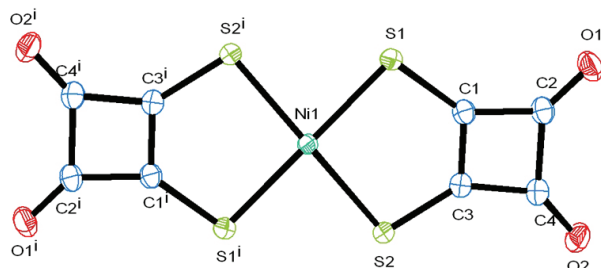


Figure 1. ORTEP plot of the complex dianion in bis(*n*-hexyltriphenylammonium)-bis(1,2-dithiosquarato)nickelate(II), (HexPh_3P)₂[Ni(dtsq)₂].

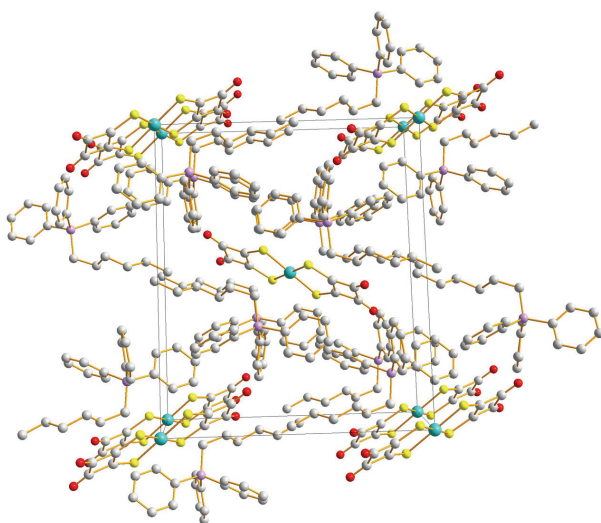


Figure 2. Packing diagram of (HexPh_3P)₂[Ni(dtsq)₂] (hydrogen atoms are omitted for clarity).

Figures 1 and 3 show the molecular structures of the complex dianions of both bis(1,2-dithiosquarato)nickelates(II), (BuPh_3P)₂[Ni(dtsq)₂] and (HexPh_3P)₂[Ni(dtsq)₂].

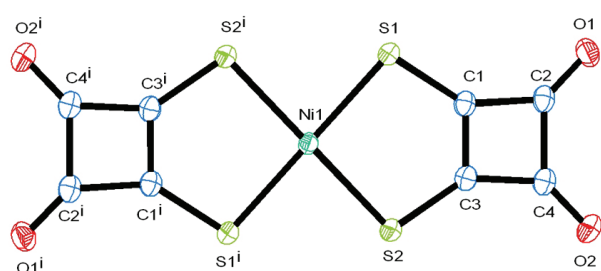


Figure 3. ORTEP plot of the complex dianion in bis(*n*-butyltriphenylammonium)-bis(1,2-dithiosquarato)nickelate(II), (BuPh_3P)₂[Ni(dtsq)₂].

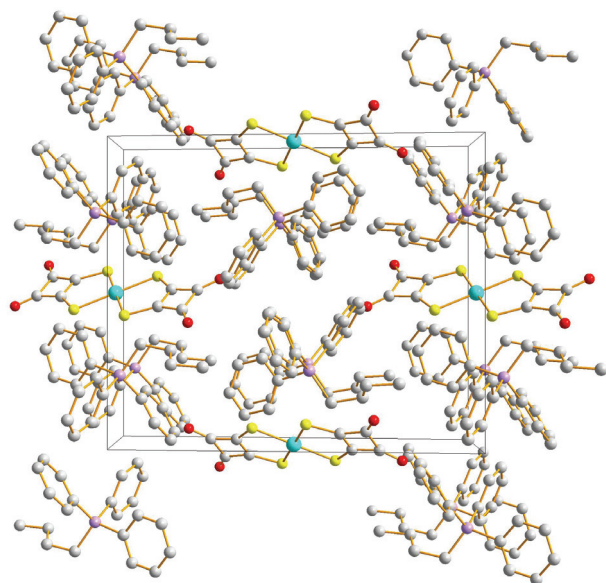


Figure 4. Packing diagram of (BuPh_3P)₂[Ni(dtsq)₂] (hydrogen atoms are omitted for clarity).

As expected the two bis(1,2-dithiosquarato)nickelate(II) dianions are in a nearly perfect square-planar NiS_4 coordination geometry. Only small differences in bond distances

Table 2. Selected bond lengths [Å] and bond angles [°] in (HexPh_3P)₂[Ni(dtsq)₂].

C(1)–S(1)	1.6937(13)	C(3)–S(2)	1.7027(13)
Ni(1)–S(1)	2.2189(3)	Ni(1)–S(2)	2.2148(3)
C(1)–C(2)	1.4833(18)	C(3)–C(4)	1.4740(18)
C(1)–C(3)	1.3775(18)	C(2)–C(4)	1.5494(19)
O(1)–C(2)–C(1)	137.26(13)	O(2)–C(4)–C(3)	137.07(13)
O(1)–C(2)–C(4)	136.17(12)	O(2)–C(4)–C(2)	136.12(12)
C(1)–C(2)–C(4)	86.57(10)	C(1)–C(3)–C(4)	93.60(11)
C(3)–C(1)–C(2)	93.01(11)	C(3)–C(4)–C(2)	86.73(10)
S(1)–C(1)–C(2)	143.16(10)	S(2)–C(3)–C(4)	142.86(10)
S(1)–C(1)–C(3)	123.80(10)	S(2)–C(3)–C(1)	123.51(10)
C(1)–S(1)–Ni(1)	98.98(5)	C(3)–S(2)–Ni(1)	98.96(4)
S(1)–Ni(1)–S(2)	94.675(12)		

Table 3. Selected bond lengths [Å] and bond angles [°] in (BuPh₃P)₂[Ni(dtsq)₂]

C(1)–S(1)	1.6916(14)	C(3)–S(2)	1.6978(14)
Ni(1)–S(1)	2.2261(4)	Ni(1)–S(2)	2.2186(3)
C(1)–C(2)	1.4858(19)	C(3)–C(4)	1.4673(19)
C(1)–C(3)	1.380(2)	C(2)–C(4)	1.539(2)
O(1)–C(2)–C(1)	137.48(14)	O(2)–C(4)–C(3)	136.63(14)
O(1)–C(2)–C(4)	135.94(13)	O(2)–C(4)–C(2)	136.09(13)
C(1)–C(2)–C(4)	86.55(11)	C(1)–C(3)–C(4)	93.44(11)
C(3)–C(1)–C(2)	92.70(11)	C(3)–C(4)–C(2)	87.26(11)
S(1)–C(1)–C(2)	143.70(11)	S(2)–C(3)–C(4)	142.71(11)
S(1)–C(1)–C(3)	123.59(11)	S(2)–C(3)–C(1)	123.81(11)
C(1)–S(1)–Ni(1)	99.11(5)	C(3)–S(2)–Ni(1)	99.02(5)
S(1)–Ni(1)–S(2)	94.406(13)		

and bond angles in the limits of significance can be detected (see Tables 2 and 3). Also the cations do not show significant effects in their structures. This situation is in full agreement with other bis(1,2-dithiosquarato)metalates.^{76–83} The bite distances (S–S) in the ligands differ only very slightly. Figures 2 and 4 show the crystal packing of both compounds, which are determined by the cations (BuPh₃P)⁺ and (HexPh₃P)⁺. Important are the intermolecular distances between the nickel ions because they might have an influence on the formation and the particle size of the products after thermal treatment. These parameters can be tuned by the selection of different cations with varying steric demands.⁸³ In these presented two structures of (BuPh₃P)₂[Ni(dtsq)₂] and (HexPh₃P)₂[Ni(dtsq)₂] the shortest intermolecular metal–metal distances are 8.9132 Å and 9.2459 Å, respectively.

3. 2. EPR Spectroscopy

For EPR spectroscopic investigations the bis(1,2-dithioquadratato)nickelates(II) of this series have been used as diamagnetic host lattices and have been doped with traces of Cu(II). Table 4 summarizes the measured EPR parameters and Figure 5 presents the EPR spectra of the two Cu(II) doped compounds (BuPh₃P)₂[Ni/Cu(dtsq)₂] and (HexPh₃P)₂[Ni/Cu(dtsq)₂]. The spectra are of axial symmetry and all g_{||}- and g_⊥-values are in a range

which is expected for square planar CuS₄-coordination geometry as it is discussed in more detail by Wenzel *et al.*⁸¹ The g_{||}- values differs only very slightly from the theoretical value, which is extracted from a single crystal measurement. This small difference might also be due to the separate measurements on two different types of EPR-spectrometers. These parameters speak for a nearly exact square planar coordination sphere in all complexes of this series, also for those where no X-ray structure determination was available (see Table 4). For the low and the high field lines in the parallel part of the axial symmetric spectrum the isotope splitting, due to the two copper isotopes, ⁶⁵Cu and ⁶³Cu with a natural abundance of 30.8% and 69.2%, respectively, is well resolved as doublets.

3. 3. TG/DTA Analysis and Thermal Treatment

Figure 6 shows the result of the thermal analysis of (HexPh₃P)₂[Ni(dtsq)₂] which is characteristic for the TG/DTA analyses of the whole series. In the thermogravimetry curve the release of some traces of surface water is followed by two main decomposition steps with significant mass loss for both steps are found. The DTA analysis exhibits an endothermic step at about 180 °C, which is in good agreement with the measured melting point at 182–184 °C. The four exothermic peaks at 279, 327, 467

Table 4. Anisotropic EPR-parameters for the investigated Cu(II) doped bis(1,2-dithioquadratato)nickelates(II) (coupling constants / · 10⁻⁴ cm⁻¹).

Complex cation	g	A	g _⊥	A _⊥	ref.
(MePh ₃ P) ⁺	2.118	158	2.029	38	
(BuPh ₃ P) ⁺	2.111	158	2.027	39	
(HexPh ₃ P) ⁺	2.110	159	2.026	40	
(BzlMe ₃ N) ⁺	2.110	160	2.026	40	
(BzlEt ₃ N) ⁺	2.122	159	2.028	37	81
(BzlBu ₃ N) ⁺	2.115	159	2.022	37	

experimental errors: g- values: ±0,003; coupling constants: ±2 · 10⁻⁴ cm⁻¹

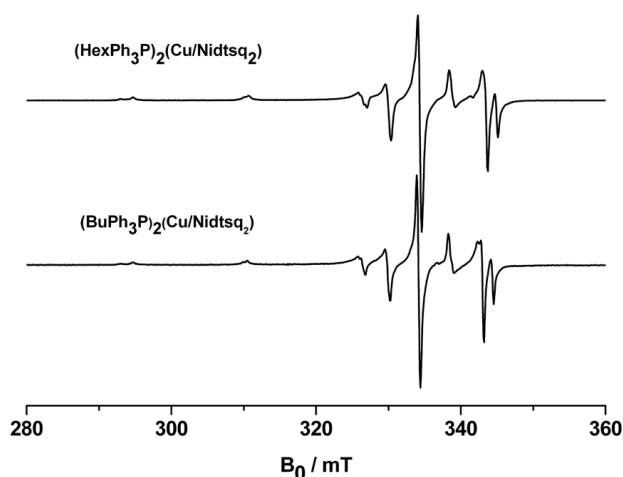


Figure 5. EPR powder spectra of the Cu(II) doped host lattices $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ and $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ ($T = 292 \text{ K}$).

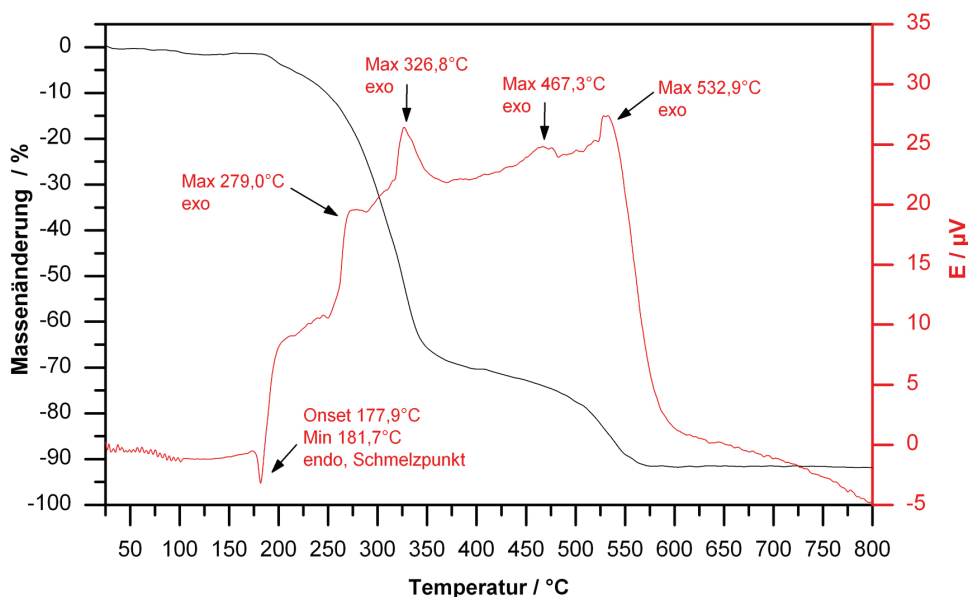


Figure 6. TG/DTA analysis of $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$.

Table 5. Residues (experimental and calculated) of the products after thermal treatment during the TG/DTA-measurements and their XRD characteristics of the series of bis(1,2-dithiosquarato)nickelates(II).

cation	XRD characteristics	residue (exp.) / %	residue (calc.) / %
in air, 50 mL min^{-1} , 800 °C , 10 K min^{-1}			
$(\text{BuPh}_3\text{P})^+$	NiO	12.0	7.6
$(\text{HexPh}_3\text{P})^+$	NiO	9.3	7.2
$(\text{BzlBu}_3\text{N})^+$	NiO	8.9	8.3
in a N_2 -atmosphäre, 30 L min^{-1} , 3 h at 650 °C , 3 K min^{-1}			
$(\text{MePh}_3\text{P})^+$	NiO	9.2	8.3
$(\text{BuPh}_3\text{P})^+$	NiO	8.3	7.6
$(\text{HexPh}_3\text{P})^+$	NiO	6.4	7.2
$(\text{BzlEt}_3\text{N})^+$	NiO	9.7	10.2

and 533 °C belong to four individual decomposition steps who might be attributed to the decomposition of the complex dianion as well as the decomposition of the „onium“ cations.

Table 5 presents the results after thermal treatment of the synthesized complexes during the DTA/TG measurements and the remaining residues compared to the calculated residues due to the XRD results. Interestingly, in all cases in air as well as under a nitrogen atmosphere, exclusively the formation of nickel oxide (NiO) can be observed as it is demonstrated in Figures 7 and 8. This was expected under normal atmospheric conditions, but it is a little surprising under a N_2 -atmosphäre. The oxygen for the formation of the nickel oxide is obviously coming from the decomposed 1,2-dithiosquarate ligands. In some samples of this series only traces of amorphous by-products might appear. Under those conditions the formation of any nickel sulfide compounds is not observed.

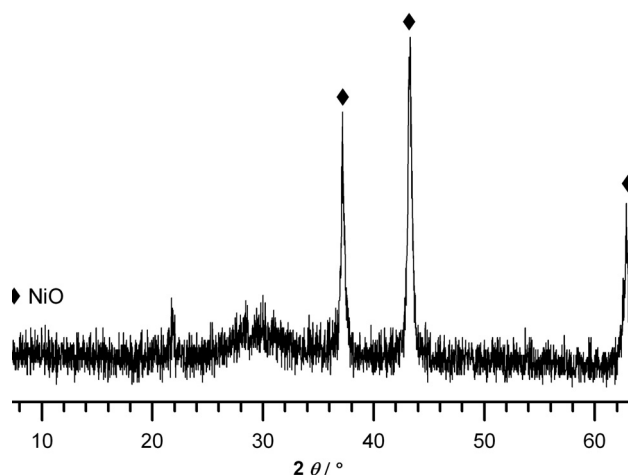


Figure 7. XRD pattern of the product after thermal treatment of $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ in air.

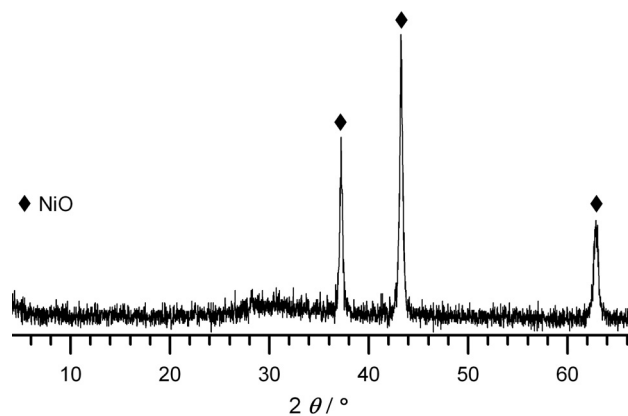


Figure 8. XRD pattern of the product after thermal treatment of $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ under a nitrogen atmosphere.

4. Conclusions

In this study, a series of new bis(1,2-dithiosquarato)nickelates(II) with different “onium” cations has been synthesized and characterized by ESI-mass spectrometry, elemental analysis and IR spectroscopy. For two complexes of the series, $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ and $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$, single crystals of diffractometer quality were obtained by slow evaporation of the solvents and the results of the X-ray structure determinations are presented. For EPR spectroscopic investigations the bis(1,2-dithioquadratato)nickelates(II) of this series were used as diamagnetic host lattices and have been doped with traces of Cu(II). The spectra are of axial symmetry and all g_{\parallel} and g_{\perp} -values are in a range which is expected for square planar CuS_4 -coordination geometry. After thermal treatment in air as well as under nitrogen atmosphere for all complexes exclusively nickel(II) oxide as product was ob-

tained. The particles were identified by XRD measurements. The product formation was studied with thermal analysis (TG/DTA).

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Povzetek

1,2-ditioskvaratonikelati nastanejo z neposredno reakcijo kovinske soli z dikalijevim ditioskvaratom v prisotnosti ustreznega kationa. V članku poročamo o sintezah in karakterizaciji, vključno z masno spektrometrijo, skupine 1,2-ditioskvaratonikelatov(II), $[\text{Ni}(\text{dtsq})_2]^{2-}$, z nekaterimi kationi. Predstavljamo tudi kristalni strukturi dveh diamagnetnih kompleksov, $(\text{HexPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$ in $(\text{BuPh}_3\text{P})_2[\text{Ni}(\text{dtsq})_2]$, ki vsebujeta sterično zahtevna »protikationa«. Z dopiranjem diamagnetnih nikljevih kompleksov s sledovi bakra(II) smo lahko posneli EPR in tako dobili dodatne strukturne informacije. Termično obnašanje spojin opisanih v tem članku smo spremljali s termogravimetrijo in diferencialno termično analizo (TG/DTA). Kot končen produkt termolize, tako na zraku kot v dušikovi atmosferi, nastajajo v vseh primerih nanodelci nikljevega oksida. Njihov nastanek smo potrdili z rentgensko praškovo difrakcijo.