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Impact of tetrahedral and square planar geometry of Ni(II) complexes with (pseudo)halide ligands to magnetic properties

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Abstract

Four tetracoordinate Ni(II) complexes have been prepared, structurally characterized, and subjected to magnetometric studies. The complexes $[Ni(PPh_3)_2(NCS)_2]$, $[Ni(dppp)(NCS)_2]$, and $[Ni(dppm)Br_2]$ are planar and thus diamagnetic. The complex $[Ni(biqu)Br_2]$ is quasi-tetrahedral, with the geometry close to C_{2v} symmetry, and paramagnetic. While on one side it resembles a prolate bisphenoid (the angle N-Ni-N = 83 deg), on the second side it mimics an oblate bisphenoid (Br-Ni-Br = 126 deg). It exhibits a zero-field splitting of the ground term ³A₂ into three crystal-field multiplets that can be described by *D* and *E* parameters within the spin Hamiltonian formalism. The *ab initio* calculations confirm this interpretation; however, the evaluation of the spin-Hamiltonian parameters meets difficulties owing to the quasi-degeneracy of the electronic terms.

Key words

Ni(II) complexes, P-donor ligands, N-donor ligands, (pseudo)halide ligands, paramagnetism, diamagnetism.

1. Introduction

Magnetic anisotropy of transition metal complexes attracts much attention in the recent period because this is a key factor that induces the slow magnetic relaxation and consequently a behavior of the metal complexes as single molecule (single ion) magnets – SMMs, SIMs. The SIM behavior has been observed among several first-row transition metal complexes such as V(IV), Cr(III), low-spin Mn(IV), Mn(III), Fe(III), Fe(I), Co(II), Ni(II), Ni(I), and Cu(II) [1-11]. Though some families are extremely rich, such as tri-, tetra-, penta-, hexa-, hepta- and octacoordinate Co(II) complexes, some are represented only by a few or a single example [12, 13]. The class of Ni(II) SIMs is limited only to three compounds so far of which [Ni(*pydca*)(*dmpy*)]·H₂O and [Ni(NCS)₂(*nqu*)₂(H₂O)₂]·2*nqu* are hexacoordinate, and [Ni(*mdabco*)₂Cl₃]ClO₄ is pentacoordinate [14, 15]. All of them possess negative axial zero-field splitting parameter D < 0 (-13.7, -5.9, and -311 cm⁻¹) as a prerequisite of the barrier to spin reversal that facilitates the SIM behavior. The class of hexacoordinate Ni(II) complexes is a widely studied and well understood case where the magnetic anisotropy parameter can be predicted and tuned on the basis of the magnetostructural D-correlation [16].

The class of tetracoordinate Ni(II) complexes is studied in a lower extent. There is one obstacle: owing to the Jahn-Teller effect the ground electronic term ${}^{3}T_{1}$ in the tetrahedral geometry is unstable and the geometry is stabilized along the e-mode of distortion leading either to the ${}^{3}A_{2}$ or ${}^{3}E$ state of the D_{2d} geometry. The latter is also unstable and the distortion continues to the stable geometry of the C_{2v} symmetry (or lower) with ${}^{3}A_{1}$, ${}^{3}B_{1}$, ${}^{3}B_{2}$ terms. Another obstacle originates in weaker crystal-field strength of the tetrahedral systems when compared to the octahedral ones: the quasi-degeneracy is a common feature since the energy gap Δ_{ax} between the ground and the first excited terms is rather low. This causes that the evaluation of the traditional spin-Hamiltonian parameters (*D* and *E*) could violate because the perturbation theory tends to diverge.

Herein, we are reporting about structural, spectral, and magnetic characterization of tetracoordinate Ni(II) complexes with various P-donor ligands, N-donor ligands and (pseudo)halide coligands: $[Ni(PPh_3)_2(NCS)_2]$ **1**, $[Ni(dppm)Br_2]$ **2**, $[Ni(biqu)Br_2]$ **3** and $[Ni(dppp)(NCS)_2]$ **4**. Our primary goal was to explore the possibilities of preparing pseudotetrahedral Ni(II) SIMs containing P-donor ligands. However, we managed to isolate diamagnetic square-planar systems as a consequence of the generated strong ligand field. Complex **3** is an analog of complex **2** containing N-donor neutral ligand with weaker field. As expected, this complex is pseudotetrahedral and hence paramagnetic.

2. Experimental

2.1. Chemicals and handling

All chemicals were purchased and used as received in reagent grade. The inorganic Ni(II) salts used in reactions were available as freshly synthesized $Ni(SCN)_2$ by changing reaction of KSCN with $NiCl_2 \cdot 6H_2O$ or in a form of anhydrous $NiCl_2$. All solids and solvents (ethanol, acetonitrile) were used without any further purification or drying. The manipulations were made under air conditions. The products were filtered over the ashless paper and fritted glass with porosity no. 4.

2.2. Physical Measurements

Elemental analyses were measured by Flash 2000 CHNS apparatus (Thermo Scientific). The samples for FT-IR measurements was not dried prior to its using and were used as freshly growth crystals. The KBr powder for FT-IR measurements was kept against absorption of moisture in the oven. The Nujol's absorption UV-Vis spectra (190 - 1100 nm) for solid samples were measured by Specord 250 Plus (Analytica Jena) with the DAD detector at room temperature. Melting points were studied with thermo-microscopy by Kofler hot-stage microscope at 4°C·min⁻¹ and reported without corrections.

2.3. Preparation of complexes

[Ni(PPh₃)₂(NCS)₂], **1**. A 100 cm³ round bottom flask was charged with triphenylphosphine (525 mg, 2 mmol) acetonitrile (15 cm³). Ligand was dissolved in 5 minutes at 60 °C. 1 cm³ of freshly synthesized Ni(NCS)₂ in half of molar equivalent was added. The reaction mixture changed color gradually to dark red. The reaction was heated for 20 hours at 80 °C. Red needles were obtained after standing for two days and filtration of mother liquid. Yield: 0.068 g. Melting point: 228 - 230°C. *Anal. Calc.* for C₃₈H₃₀N₂P₂NiS₂ (699.41g·mol⁻¹): C, 65.25; H, 4.32; N, 4.01; S, 9.17. Found: C, 64.91; H, 4.25; N, 4.01; S, 9.17. Selected IR bands (1.4 mg/250 mg KBr) v/cm⁻¹: 3060(w), 2085(s) $v_{as(CN from NCS)}$, 1479(m), 1434(s), 1308(w), 1178(w), 1096(s), 1024(w), 997(w), 867(m), 750(s), 744(w), 707(w), 693(s), 524(s), 512(m), 497(m), 457(w), 414(w) (s = strong, m = medium, w = weak). UV/Vis (Nujol) $v_{max}/10^3$ cm⁻¹ (relat. absorb.): 24.04 (1.112), 19.46 (0.666).

100 cm^3 round bottom [Ni(dppm)Br₂], 2. А flask was charged with bis(diphenylphosphino)methane (150 mg, 0.39 mmol), and dissolved in acetonitrile (20 cm³). NiBr₂ (85.2 mg, 0.39 mmol) was added into the solution and color changed immediately to dark red. Mixture was stirred for 4 hours with intensive reflux. Red-block crystals were isolated after 3 days by filtration. Melting point: > 200°C. Anal. Calc. for $C_{25}H_{22}Br_2NiP_2$ (602.89 g·mol⁻¹): C, 49.80; H, 3.68. Found: C, 49.74; H, 3.59. IR bands v/cm⁻¹: 3350(w), 3051(w), 2953(w), 2681(w), 2581(w), 2322(w), 2198(w), 1583(w), 1568(w), 1479(m), 1432(s), 1335(m), 1307(m), 1182(m), 1157(m), 1097(s), 1075(m), 1024(m), 997(s), 924(w), 843(w), 740(m), 730(s), 712(m), 685(s), 653(m), 616(w), 539(s), 497(s), 476(m), 438(m) (s = strong, m = medium, w = weak). UV/Vis (Nujol) $v_{\text{max}}/10^3$ cm⁻¹ (relat. absorb.): 16.86 (0.532), 20.33 (0.809).

[Ni(*biqu*)Br₂], **3**. A mixture consisting of 0.109 g of NiBr₂ (0.5 mmol) and 0.128 g of *biqu* (0.5 mmol) in 15 cm³ of ethanol was placed into teflon-lined steel autoclave and heated to 120 °C for 16 h. Red crystals formed in the solution upon slow cooling of the mixture to the room temperature.

Crystals were separated by filtration, rinsed with cold ethanol and dried in air. *Anal. Calc.* for $C_{18}H_{12}Br_2N_2Ni$ (474.80 g·mol⁻¹): C, 45.53; H, 2.55; N, 5.90. Found: C, 45.25; H, 2.51; N, 5.86. IR bands v/cm⁻¹: 3086(w), 3055(w), 1965(w), 1934(w), 1822(w), 1586(m), 1508(s), 1434(m), 1380(m), 1366(w), 1341(w), 1302(w), 1214(m), 1145(s), 1106(m), 978(w), 957(w), 870(m), 829(s), 780(s), 746(s), 699(w), 659(w), 637(w), 526(w), 499(w), 487(s) (s = strong, m = medium, w = weak). UV/Vis (Nujol) $v_{max}/10^3$ cm⁻¹ (relat. absorb.): 9.86 (0.282), 11.05 (0.246), 11.42 (0.247), 15.63 (0.225), 19.19 (0.481).

 cm^3 round bottom 50 flask $[Ni(dppp)(NCS)_2],$ 4 А was charged with bis(diphenylphosphino)propane (177 mg, 0.43 mmol) and acetonitrile (20 cm³) as solvent. $Ni(SCN)_2$ (75 mg, 0.43 mmol) in ethanolic solution was added into the clear solution and color changed immediately to yellow-brown. Mixture was stirred for 3 hours with intensive reflux. Yellow crystals were isolated after 2 days of controlled evaporation at room temperature. Selected IR bands v/cm⁻¹: 3159,(w), 3053(w), 2926(w), 2686(w), 2074(s) v_{as(CN from NCS)}, 1965(w), 1815(w), 1678(w), 1585(w), 1483(m), 1435(s), 1408(m), 1315(w), 1306(w), 1101(s), 996(m), 944(m), 832(m), 747(m), 719(m), 704(s), 686(s), 559(m), 554(s), 477(m), 457(s), 439(m) (s = strong, m = medium, w = weak). UV/Vis (Nujol) $v_{max}/10^3$ cm⁻¹ (relat. absorb.): 9.86 (0.282), 11.05 (0.246), 11.42 (0.247), 15.63 (0.225), 19.19 (0.481). UV/Vis (Nujol) $v_{max}/10^3$ cm⁻¹ (relat. absorb.): 23.75 (0.779)

2.4. X-ray crystal structure determination

Data collection and cell refinement of suitable single crystals of 1, 2 and 4 were made by Stoe StadiVari diffractometer using PILATUS3R 300K HPAD detector and micro-focused source Xenocs Genix3D with CuK α at 100K. Corrections to Lorentz, polarization and multi-scan absorption effects were applied. The structure was solved by charge-flipping method and refined anisotropically by common least-squares methods. The programs SUPERFLIP or SHELXT, SHELXL (vers. 2014/7 or 2018/3), OLEX2 and MERCURY have been used for structure determination, refinement and drawing [17-19]. The hydrogen atoms were refined with fixed distances from the parent carbon atoms. Selected crystal data are presented in Table 1.

One of the phenyl groups [C1–C6/C1A–C6A] of **2** is disorderd with occupancy factors 0.537(7) and 0.463(7), respectively.

| | [Ni(PPh ₃) ₂ (NCS) ₂], 1 | [Ni(<i>dppm</i>)Br ₂], 2 | $[Ni(dppp)(NCS)_2], 4$ |
|--------------------------------------|--|---|--------------------------------|
| Empirical formula | $C_{38}H_{30}N_2P_2NiS_2$ | $C_{25}H_{22}Br_2NiP_2$ | $C_{29}H_{26}N_2P_2NiS_2$ |
| Formula weight $/g \text{ mol}^{-1}$ | 699.41 | 602.89 | 587.29 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | <i>P</i> -1 | <i>I</i> 2 | <i>C</i> 2/c |
| Temperature /K | 100 | 100 | 100 |
| Crystal size /mm | $0.21 \times 0.12 \times 0.06$ | $0.38 \times 0.35 \times 0.25$ | $0.26 \times 0.17 \times 0.08$ |
| Z | 1 | 2 | 4 |
| <i>a</i> / Å | 7.8813(5) | 11.9829(3) | 24.1817(7) |
| b / Å | 10.3849(7) | 7.4780(2) | 9.0253(3) |
| <i>c</i> / Å | 11.4155(8) | 13.6265(4) | 14.6344(4) |
| $\alpha /^{\circ}$ | 68.742(5) | 90 | 90 |
| β /° | 74.235(5) | 106.522(2) | 120.762(2) |
| γ /° | 88.129(5) | 90 | 90 |
| V/Å ³ | 835.73(10) | 1170.63(6) | 2744.53(15) |
| $\rho_{\rm calc}/{\rm g~cm}^{-3}$ | 1.390 | 1.710 | 1.421 |
| μ / mm^{-1} | 3.140 | 6.557 | 3.706 |
| <i>F</i> (000) | 362.0 | 600.0 | 1216.0 |
| Radiation | CuKa | CuKa | CuKα |
| | $(\lambda = 1.54186)$ | $(\lambda = 1.54186)$ | $(\lambda = 1.54186)$ |
| 2Θ range for data | 8.656 to 141.354 | 8.686 to 142.508 | 8.510 to 142.762 |
| collection/° | | | |
| Index ranges | $-9 \le h \le 9,$ | $-12 \le h \le 14$, | $-24 \le h \le 29$, |
| | $-10 \le k \le 12$, | $-9 \le k \le 6,$ | $-11 \le k \le 9,$ |
| | $-7 \le l \le 13$ | $-16 \le l \le 16$ | $-15 \le l \le 17$ |
| Data/restraints/parameters | 3072/0/206 | 1883/188/133 | 2620/0/73 |
| Goodness-of-fit on F^2 | 1.070 | 1.050 | 1.053 |
| Final R indexes [I>= 2σ | $R_1 = 0.0400,$ | $R_1 = 0.0306,$ | $R_1 = 0.0290,$ |
| (I)] | $wR_2 = 0.1118$ | $wR_2 = 0.0805$ | $wR_2 = 0.0751$ |
| R indices (all data) | $R_1 = 0.0439,$ | $R_1 = 0.0308,$ | $R_1 = 0.0317,$ |
| | $wR_2 = 0.1144$ | $wR_2 = 0.0807$ | $wR_2 = 0.0771$ |
| color | red | red | yellow |
| CCDC No. | 1585156 | 1585157 | 1844141 |

Table 1. Crystal data and structure refinement for complexes under study.

2.5. Magnetic data collection

The magnetic data was collected by SQUID apparatus (MPMS-XL7/evercool, Quantum Design) with samples encapsulated in the diamagnetic gelatin holder. The DC data was acquired in the RSO mode of detection at $B_{\rm DC} = 0.1$ T. Raw magnetic data was corrected for underlying magnetism and presented either as the effective magnetic moment. The magnetization data was taken at two temperatures, T = 2.0 and 4.6 K, up to B = 7 T.

2.6. Quantum-chemical calculations

Ab initio calculations were performed with ORCA 4.0.0 computational package at the experimental geometries [20]. The relativistic effects were included in the calculations with zero order regular approximation (ZORA) together with the scalar relativistic contracted version of def2-TZVPP basis functions for the Ni atom and def2-SV(P) basis functions for other elements. The calculations were based on state average complete active space self-consistent field (SA-CASSCF) wave functions complemented by N-electron valence second order perturbation theory (NEVPT2) [21]. The active space comprised of eight electrons in ten metal-based d-orbitals (including the double-shell effect). The state averaged approach was used, in which 10 triplet and 15 singlet states were equally weighted. The calculations utilized the RI approximation with appropriate decontracted auxiliary basis set and the chain-of-spheres (RIJCOSX) approximation to exact

exchange. Increased integration grids (Grid4 and GridX5) and tight SCF convergence criteria were used. Energies of multiplets were calculated through quasi-degenerate perturbation theory in which an approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) was utilized [22]. The ZFS parameters were calculated using the effective Hamiltonian theory.

3. Results and discussion

3.1. Structural data

The complex **1** crystallized in the triclinic system with the space group P-1. Perspective view on the molecular structure of **1** is displayed in Fig. 1. The chromophore {NiP₂N₂} belongs to square planar shape formed by central Ni(II) atom surrounded by two nitrogen atoms of isothiocyanato groups (-NCS) and two phosphorus atoms of two triphenylphospine ligands in *trans* positions. The Ni1 atom lies in special position of centre of symmetry. The bond distances between Ni–P are identical (2.24 Å) and much shorter than Ni–N by 0.41 Å (Table 2). One type of intermolecular contact was identified as C···H-C. Considering of the square planar geometry, two bond angles P1ⁱ-Ni1-P1 and N1-Ni1-N1ⁱ lies on 180°, whereas other angles have 92.13° and 87.87°, respectively (Table 2).

The complex 2 crystallized in the monoclinic system with the non-centrosymmetric space group *I*2. Perspective view on the molecular structure of 2 is displayed in Fig. 1. Red color of this complex has been well predicted its square planar geometry. The chromophore {NiP₂Br₂} is composed by two atoms of phosphorus from one chelating bis(diphenylphosphino)methane ligand and two bromine atoms. The Ni1 atom and methylene carbon atom (C13) of *dppm* lie on 2-fold axis. The bond distances between Ni–P are 2.14 Å and between Ni–Br are 2.35 Å. The angle Br1-Ni1-Br1ⁱⁱ lies on 99.8°, in comparison of P1-Ni1-P1ⁱⁱ which is 75.9° (Table 3).

The crystal structure of **3** has been determined by Butcher & Sinn [23]. The complex crystallizes in the monoclinic system with the centrosymmetric space group $P2_1/c$. The complex **3** is quasi-tetrahedral, with the geometry close to C_{2v} symmetry. The Ni–Br bond distances are 2.33 and 2.35 Å, and both Ni–N bond lenghts are 1.99 Å (Table 4).

The complex **4** crystallized in the monoclinic system with the centrosymmetric space group C2/c. Molecular structure of **4** is drawn in Fig. 1. The chromophore {NiP₂N₂} belongs to square planar shape formed by central Ni(II) atom surrounded by two nitrogen atoms of isothiocyanato groups (-NCS) and two phosphorus atoms of bis(diphenylphosphino)propane ligand. The Ni1 atom and one methylene carbon atom of propylene group of *dppp* (C13) lie on 2-fold axis. The bond distances between Ni–P are identical (2.26 Å) and between Ni–N are also identical (1.88 Å, Table 2). Considering of the square planar geometry in *cis* configuration, two bond angles P1ⁱⁱⁱ-Ni1-P1 and N1-Ni1-N1ⁱⁱⁱ are 89.9° and 93.1°, respectively (Table 5).





[Ni(PPh₃)₂(NCS)₂], 1

 $[Ni(dppm)Br_2], 2$





[Ni(*biqu*)Br₂], **3** (refcode NIBRBQ)

| Br2 Br: | le le | NT NT | ۵ | |
|--|------------------------|---------------------------------------|--------------------------------|---|
| [Ni(<i>biqu</i>)Br ₂ (refcode NIBR |], 3 [Ni BQ) | i(<i>dppp</i>)(NCS) ₂], | 4 | R |
| Fig. 1. Perspective | e views of the Ni(II | I) complexes 1-4 | 4. | |
| Table 2. Selected | bond lengths (Å) a | nd bond angles | (°) in chromophore of 1 | |
| Ni1-P1 | 2.2421(5) | P1 ⁱ –Ni1–P1 | 180.0 | |
| Ni1-P1 ⁱ | 2.2421(5) | N1–Ni1–P1 ⁱ | 92.13(5) | |
| Ni1-N1 ⁱ | 1.829(2) | N1-Ni1-P1 | 87.87(5) | |
| Ni1-N1 | 1.829(2) | N1 ⁱ –Ni1–P1 | 92.13(5) | |

| Ni1-P1 | 2.2421(5) | P1 ⁱ –Ni1–P1 | 180.0 |
|---------------------|-----------|--------------------------------------|----------|
| Ni1-P1 ⁱ | 2.2421(5) | N1–Ni1–P1 ⁱ | 92.13(5) |
| Nil-Nl ⁱ | 1.829(2) | N1-Ni1-P1 | 87.87(5) |
| Nil-Nl | 1.829(2) | N1 ⁱ –Ni1–P1 | 92.13(5) |
| | | N1 ⁱ –Ni1–P1 ⁱ | 87.87(5) |
| | | N1–Ni1–N1 ⁱ | 180.0 |

Symmetry code: (i) 1-x, 1-y, 2-z

| Ni1–Br1 | 2.3454(9) | Br1 ⁱⁱ –Ni1–Br1 | 99.77(5) | |
|-----------------------|------------|---|-----------|--|
| Ni1–Br1 ⁱⁱ | 2.3454(9) | P1–Ni1–Br1 | 92.44(4) | |
| Ni1–P1 | 2.1423(16) | P1–Ni1–Br1 ⁱⁱ | 166.74(5) | |
| Ni1–P1 ⁱⁱ | 2.1423(16) | P1 ⁱⁱ –Ni1–P1 | 75.95(8) | |
| | | P1 ⁱⁱ –Ni1–Br1 | 166.74(5) | |
| | | P1 ⁱⁱ –Ni1–Br1 ⁱⁱ | 92.44(4) | |
| | | | | |

Symmetry code: (ii) -x, y, 1-z

| Table 4. Selected bond lengths (Å) and bond angles (°) in chromophore of 3 . | |
|---|--|
|---|--|

| Ni1–Br1 | 2.331(1) | Br1-Ni1-Br2 | 124.94(4) | |
|---------|----------|-------------|-----------|--|
| Ni1–Br2 | 2.351(1) | N1-Ni1-Br1 | 109.5(2) | |
| Ni1–N1 | 1.991(5) | N1-Ni1-Br2 | 111.8(2) | |
| Ni1–N2 | 1.993(5) | N1-Ni1-N2 | 82.6(2) | |
| | | N2-Ni1-Br1 | 115.5(2) | |
| | | N2-Ni1-Br2 | 104.5(2) | |
| | | | | |

| Table 5. Selected bond lengths (A) and bond angles (°) in chromophore of 4. | | | | | |
|---|-----------|--|-----------|--|--|
| Ni1–P1 | 2.1594(5) | P1–Ni1–P1 ⁱⁱⁱ | 89.92(2) | | |
| Ni1–P1 ⁱⁱⁱ | 2.1594(5) | N1–Ni1–P1 | 173.98(4) | | |
| Ni1–N1 | 1.885(1) | N1–Ni1–P1 ⁱⁱⁱ | 88.77(4) | | |
| Ni1–N1 ⁱⁱⁱ | 1.885(1) | N1–Ni1–N1 ⁱⁱⁱ | 93.12(8) | | |
| | | N1 ⁱⁱⁱ –Ni1–P1 | 88.77(4) | | |
| | | N1 ⁱⁱⁱ –Ni1–P1 ⁱⁱⁱ | 173.98(4) | | |

Symmetry code: (iii) 1–*x*, *y*, 3/2–*z*

3.2. Electronic spectra

Solid state electronic spectra (measured in Nujol mull) of the studied complexes are shown in Fig. 2. Red tetracoordinate complexes [Ni(PPh₃)₂(NCS)₂], 1; [Ni(*dppm*)Br₂], 2; [Ni(*biqu*)Br₂], 3 and $[Ni(dppp)(NCS)_2]$, 4 show relatively intense d-d bands in the range of 10 000 – 26 000 cm⁻¹ (Table 6). In square-planar complexes 1, 2 and 4 a diamagnetic ground term ${}^{1}A_{1g}$ is stabilized as a consequence of increased ligand-field strength to the detriment of vacant axial positions. Following transitions can be identified: 19 462 cm⁻¹ (${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$), 24 047 cm⁻¹ (${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$) in the complex **1**, 20 332 cm⁻¹ (${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$) in the complex **2** and 23 753 (${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$) in the complex **4**. The complex **3** possess a nearly tetrahedral structure (close to D_{2d} or C_{2v}) showing the d-d transitions at 9 863 cm⁻¹ (${}^{3}A_{2} \leftarrow {}^{3}T_{1}$), 15 637 cm⁻¹ and 19 193 cm⁻¹ (${}^{3}T_{1}(P) \leftarrow {}^{3}T_{1}$). The splitting of

the second band is a consequence of the symmetry lowering. Intense charge transfer bands are located above 26 000 cm⁻¹.



Fig. 2. a) Solid state electronic spectra of complexes 1-4. b) General view of spin allowed d-d transitions in tetrahedral (left) and square-planar (right) Ni(II) complexes – not in scale.

Table 6. Electronic transitions assignment in complexes 1 through 4

| Compound | Electronic transitions /cm ⁻¹ |
|---|--|
| 1 ^b | 19 462 (${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$), 24 047 (${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$) |
| 2 ^b | $20\ 332\ (^{1}A_{2g}\leftarrow ^{1}A_{1g})$ |
| 3 ^a | 9 863 (${}^{3}A_{2} \leftarrow {}^{3}T_{1}$), 15 637, 19 193 (${}^{3}T_{1}(P) \leftarrow {}^{3}T_{1}$) |
| 4 ^b | 23 753 (${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$) |
| $[NiCl_4]^{2-a,c}$ | $E_0({}^{3}T_1); E_1({}^{3}T_2) \ 3 \ 500; E_2({}^{3}A_2) \ 6 \ 650 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 - 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 15 \ 240 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ 250 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ (\varepsilon = 21); E_3({}^{3}T_1(P)) \ 14 \ (\varepsilon = 21); E_3({}^{3}T_1(P))$ |
| | 160) with multiplet splitting; $E({}^{1}E)$ 11 630 ($\varepsilon = 6$); $E({}^{1}T_{2})$ 19 800; $10Dq = \Delta_{T} =$ |
| | $3850 \text{ cm}^{-1}, B = 725 \text{ cm}^{-1}, C = 3262 \text{ cm}^{-1}$ |
| $\left[\operatorname{Ni}(\operatorname{CN})_4\right]^{2-\operatorname{b},\operatorname{d}}$ | $E_0({}^{1}A_{1g}); E_2({}^{1}B_{1g}) 31 100, E_3({}^{2}E_g) 31 650$ |
| a | |

^a Assignments in T_d symmetry. ^b Assignments in D_{4h} symmetry. ^c [24]. ^a [25].

3.3. Modeling by the generalized crystal field theory

A regular tetrahedral Ni(II) complex possesses the ground electronic term ${}^{3}T_{1}$ that is orbitally three-fold degenerate. Owing to the Jahn-Teller effect this geometry is unstable and it is a subject of the distortion along the e+t₂ vibrational modes. Distortions along the e-mode lead to the bisphenoid of the D_{2d} symmetry that can be either prolate (elongated, two angles L-Ni-L < 109.5 deg) or oblate (compressed, two angles L-Ni-L > 109.5 deg; in the limiting case the square geometry is obtained) - Fig. 3. The prolate bisphenoid possesses the orbitally non-degenerate ground term ${}^{3}A_{2}$ and the

first excited term ³E; the spin-orbit coupling then yields the crystal field multiplets Γ_1 (ground) and Γ_5 (excited) separated by a gap $\delta_1 = D$, that is the traditional zero-field splitting within the double group D₂². On the contrary, the oblate bisphenoind possesses the orbitally degenerate ground term ³E that is further split by the spin-orbit coupling to a set of multiplets: Γ_1 , Γ_2 , Γ_5 , Γ_3 , and Γ_4 ; this situation is outside the applicability of the spin Hamiltonian formalism so that nothing like *D* and *E* parameters are meaningful.



Fig. 3. Ground electronic terms and multiplets for the prolate (left) and oblate (right) geometries of a homoleptic tetracoordinate Ni(II) complex of the D_{2d} symmetry as modelled by the GCFT.

The above considerations result from the quantitative calculations using the Generalized Crystal-Field Theory (GCFT); its principles are described elsewhere [26, 27]. A modelling of the temperature dependence of the magnetic susceptibility (converted to the effective magnetic moment) and the field dependence of the magnetization per formula unit is displayed in Fig. 4.



Fig. 4. Modeling of the magnetic functions for a homoleptic tetracoordinate Ni(II) complex. For the weak crystal field the pole strengths were $F_4 = 5000 \text{ cm}^{-1}$; for the strong crystal field $F_4 = 15000 \text{ cm}^{-1}$; $F_2 = 1.5 F_4$ are used. Magnetization per formula unit is calculated for T = 2.0 K.

In both cases the magnetic functions resemble the behaviour of a zero-field splitting system: on cooling the effective magnetic moment slightly decreases from its room-temperature value and then

it drops down to the zero. The magnetization per formula unit is almost linear until B = 7 T and much lower than the spin-only value of $M_1 = M_{mol}/N_A = 2.0 \ \mu_B$. The calculated magnetic parameters are collected in Table 7 though only the first case of the D_{2d}(p) allows an evaluation of them by means the perturbation theory. Because the first excitation energy is low, $\Delta_{ax} = 1400 \text{ cm}^{-1}$, this case need be considered as quasidegenarate. Therefore it is not surprising that the calculated value of $D/hc = 284 \text{ cm}^{-1}$ is much different from the exact multiplet splitting $\delta_1/hc = 181 \text{ cm}^{-1}$.

| Table 7. Calcula | ieu magnetik | , param | eleis | | | | |
|--|-------------------|------------|------------|-------|------------------------------------|------------------------|---------------------|
| Geometry | Spin Hamil | ltonian | paramet | ers | | Excitation energy | Multiplet gap |
| | D/hc | E/hc | g_x, g_y | g_z | χ _{TIM} /10 ⁻⁹ | $ \Delta_{\rm ax} /hc$ | δ_1/hc |
| | /cm ⁻¹ | $/cm^{-1}$ | | | $m^3 mol^{-1}$ | /cm ⁻¹ | $/\mathrm{cm}^{-1}$ |
| D _{2d} (p), GCFT ^a | 284 | - | 3.803 | 2.0 | 12.5 | 1400 | 181 |
| D _{2d} (o), GCFT ^a | undefined | - | 2.852 | 2.546 | 7.78 | 1600 | 126 |
| 3 , GCFT ^b | 40.8 | 3.5 | 2.638 | 2.401 | 5.94 | 3308 | 27.6 |
| | | | 2.682 | | | 4308 | 35.0 |
| 3 , ab initio | -49 | 10 | 2.271 | 2.697 | | 2438 | 20.7 |
| | | | 2.440 | | | 3450 | 59.2 |
| 3 , fitting | 16.5 | 5.3 | 2.321 | 2.0 | 1.3 | | |
| | | | 2.417 | | | | |

^a A homoleptic complex in a weak crystal field. ^b Combined weak (Br) and intermediate (N) crystal field.

The complex **3** in one side resembles the prolate disphenoid (angle N-Ni-N = 82 deg, a compression by -27 deg), however, on the second side it matches the oblate disphenoid (Br-Ni-Br = 126 deg, an expansion by 17 deg). The experimental geometry of the {NiN₂Br₂} chromophore has been used in the GCFT calculations with the pole strengths $F_4(Br) = 5000 \text{ cm}^{-1}$ and $F_4(N) = 8000 \text{ cm}^{-1}$. On the symmetry descent to the real C₁ symmetry the mother ground term T₁(T_d) splits into three orbitally non-degenerate daughter terms; their energies are at {0, 3308, 4308} cm⁻¹ which resembles the situation close to the prolate bisphenoid with the ground ³A₂ and excited ³E terms. Therefore it can be expected that the spin-Hamiltonian formalism is applicable, predicting D > 0.

3.4. Ab initio calculations

Table 7 Coloulated

The *ab initio* calculation at the CASSCF/NEVPT2 level predict the lowest excitation energies $\Delta_1 = 2438$ and $\Delta_2 = 3450$ cm⁻¹. These arise from the splitting of the mother tetrahedral ground term ${}^{3}T_{1}$ into daughter terms (${}^{3}A_{2}$, ${}^{3}E$) on symmetry lowering to D_{2d} and further to C_{2v}. Three daughter terms {0, 2438, 3450 cm⁻¹} can be considered as quasi degenerate so that an application of the perturbation theory in evaluating the spin-Hamiltonian parameter might be problematic. The lowest spin-orbit corrected energy levels lie at {0, 20.7 (δ_1), 59.2 (δ_2)}, {2910, 2933, 3104}, and {4170, 4173, 4252} cm⁻¹ where the square brackets collect the crystal field multiplets arising from the crystal field terms. By applying $\delta_1 = D - E$ and $\delta_2 = D + E$ one gets D = 39.9 and E = 19.3 cm⁻¹ (Fig. 5). However, a reverse situation, $\delta_1 = 2E$ and $\delta_2 = -D - E$ yields D = -69.6 and E = 10.4 cm⁻¹ (E/D = 0.18). Effective Hamiltonian spin-orbit coupling contribution gave the zero-field splitting parameters D = -48.8 cm⁻¹, E/D = 0.21 and the g-factors {2.271, 2.440, 2.697}.

The calculated *ab initio* value of $D = -48.8 \text{ cm}^{-1}$, contradicts the theoretical expectations based upon GCFT method that predicts positive value for D-parameter. An inspection to the contributions to the zero-field splitting parameters from individual excitations (see Table S1) confirms that Dvalue is dominated by the first excitation energy $\Delta_1 = 2438 \text{ cm}^{-1}$ with the increment -128 cm^{-1} . This is an overestimated value due to the failure of the perturbation theory.



Fig. 5. The lowest energy levels on symmetry lowering from elongated (prolate) bisphenoid for d⁸ systems.



Fig. 6. Modeling of the magnetic functions for **3** at the CASSCF/NEVPT2 level. Magnetization per formula unit is calculated for T = 2.0 K.

3.5. Magnetic data

Three tetracoordinate Ni(II) complexes are almost planar and thus diamagnetic. These are: $[Ni(PPh_3)_2(NCS)_2]$, **1**; $[Ni(dppm)Br_2]$, **2**; and $[Ni(dppp)(NCS)_2]$, **4**. The available magnetic data are deposited in ESI.

The quasi-tetrahedral complex [Ni(*biqu*)Br₂], **3**, is a paramagnetic species (Fig. 7). It possesses the room-temperature value of the effective magnetic moment $\mu_{eff} = 3.26 \ \mu_B$ which decreases only slightly down to 50 K; on further cooling a sharp drop occurs and $\mu_{eff} = 1.35 \ \mu_B$ at T = 1.9 K. This indicates positive zero-field splitting, D > 0. Magnetization per formula unit adopts a value of $M_1 =$ 1.12 at T = 2.0 K and B = 7.0 T which also confirms large value of the zero-field splitting.

The DC magnetic data was fitted by the standard model of the zero-field splitting

$$\hat{H}_{k,l} = D(\hat{S}_{z}^{2} - \hat{S}^{2} / 3)h^{-2} + E(\hat{S}_{x}^{2} - \hat{S}_{y}^{2})h^{-2} + \mu_{B}B_{m}(g_{x}\sin\theta_{k}\cos\varphi_{l}\hat{S}_{x} + g_{y}\sin\theta_{k}\sin\varphi_{l}\hat{S}_{y} + g_{z}\cos\theta_{k}\hat{S}_{z})h^{-1}$$
(1)

Simultaneous fitting of the susceptibility and magnetization data gave the following set of magnetic parameters referring to the spin-Hamiltonian formalism: $g_z = 2.002$, $g_x = 2.321$, $g_y = 2.417$, D/hc = +16.5 cm⁻¹, E/hc = 5.3 cm⁻¹, zj/hc = -0.15 cm⁻¹ (molecular-field corrections) and temperature-independent magnetism $\chi_{\text{TIM}} = 1.3 \times 10^{-9}$ m³ mol⁻¹ [discrepancy factors of the fit $R(\chi) = 0.032$, R(M) = 0.093]. The magnetic parameters qualitatively fulfill the consistency criterion according to which $D \sim \lambda(g_z - g_x)/2$, so that $g_z < g_x$ implies D > 0 ($\lambda/hc = -315$ cm⁻¹). The fitting with D < 0 was not successful (see Fig. S3 in ESI). The fitted value of the axial zero-field splitting parameter D matches the range expected on the basis of the GCFT model.



Fig. 7. Magnetic functions for 3. Left – temperature dependence of the effective magnetic moment (inset: molar magnetic susceptibility); right – field dependence of the magnetization per formula unit. Lines – fitted.

4. Conclusions

Four tetracoordinate Ni(II) complexes, **1** [Ni(PPh₃)₂(NCS)₂], **2** [Ni(*dppm*)Br₂], **3** [Ni(*biqu*)Br₂] and **4** [Ni(*dppp*)(NCS)₂], have been structurally, spectrally and magnetically characterized. Complexes **1**, **2** and **4** are planar diamagnetic, while the complex **3** is quasi-tetrahedral paramagnetic. Electronic structure and magnetic properties of the paramagnetic complex **3** have been subjected to deep experimental and theoretical analysis. It exhibits a zero-field splitting of the ground term quantified by a sizeable positive *D*-value. The GCFT and *ab initio* calculations confirm presence of the nondegenerate ³A₂ ground term as a consequence of the significantly distorted structure (prolate bisphenoid on one side and oblate bisphenoid on the second side).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/. CCDC nos. 1585156-1585157, and 1844141 contains the crystallographic data 4. These of for 1-2 and data can be obtained free charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Highlights:

- Four tetracoordinate Ni(II) complexes have been prepared.
- The complexes [Ni(PPh₃)₂(NCS)₂], [Ni(*dppp*)(NCS)₂], and [Ni(*dppm*)Br₂] are planar and diamagnetic.
- The complex $[Ni(biqu)Br_2]$ is pseudotetrahedral and paramagnetic.
- It exhibits a zero-field splitting of the ground term ${}^{3}A_{2}$ into three crystal-field multiplets that can be described by *D* and *E* parameters within the spin Hamiltonian formalism.

• The GCFT and *ab initio* calculations confirm this interpretation.



Four tetracoordinate Ni(II) complexes have been prepared, structurally characterized, and subjected to magnetometric studies. The complexes $[Ni(PPh_3)_2(NCS)_2]$, $[Ni(dppp)(NCS)_2]$, and $[Ni(dppm)Br_2]$ are planar and thus diamagnetic. The complex $[Ni(biqu)Br_2]$ is pseudotetrahedral, with the geometry close to C_{2v} symmetry, and paramagnetic.