

Electronic structure of  $(MePh_3P)_2[Ni^{II}(bdtCl_2)_2]$ -2(CH<sub>3</sub>)<sub>2</sub>SO and  $(MePh_3P)[Ni^{III}(bdtCl_2)_2]$  (bdtCl<sub>2</sub> = 3,6-dichlorobenzene-1,2-dithiolate)

Julia Adamko Koziskova,<sup>a</sup> Yu-Sheng Chen,<sup>b</sup> Su-Yin Grass,<sup>b</sup> Yu-Chun Chuang,<sup>c</sup> I-Jui Hsu,<sup>d</sup> Yu Wang,<sup>e</sup> Martin Lutz,<sup>f</sup> Anatoliy Volkov,<sup>g</sup> Peter Herich,<sup>a</sup> Barbora Vénosová,<sup>a,h</sup> Ingrid Jelemenská,<sup>a,i</sup> Lukáš Bučinský,<sup>a</sup> Martin Breza<sup>a</sup> and Jozef Kožíšek<sup>a</sup>\*

<sup>a</sup>Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava, SK-81237, Slovakia, <sup>b</sup>NSF's ChemMATCARS, The University of Chicago, Lemont, IL 60439, USA, <sup>c</sup>National Synchrotron Radiation Center, Hsinchu, 30076, Taiwan, <sup>d</sup>Department of Molecular Science and Engineering, Research and Development Center for Smart Textile Technology, National Taipei University of Technology, Taipei, 10608, Taiwan, <sup>e</sup>Department of Chemistry, National Taiwan University, Tapei, 10617, Taiwan, <sup>f</sup>Structural Biochemistry, Bijvoet Centre for Biomolecular Research, Utrecht University, Utrecht, 3584 CH, The Netherlands, <sup>g</sup>Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132, USA, <sup>h</sup>Department of Physics, Faculty of Science, University of Ostrava, 30.dubna 22, Ostrava, 70103, Czech Republic, and <sup>i</sup>Department of Chemistry, Faculty of Natural Sciences, Constantine the Philosopher University in Nitra, Tr. Andreja Hlinku 1, Nitra, Slovakia. \*Correspondence e-mail: jozef.kozisek@stuba.sk

High-resolution X-ray diffraction experiments, theoretical calculations and atom-specific X-ray absorption experiments were used to investigate two nickel complexes,  $(MePh_3P)_2[Ni^{II}(bdtCl_2)_2]\cdot 2(CH_3)_2SO$  [complex (1)] and  $(MePh_3P)$ -[Ni<sup>III</sup>(bdtCl\_2)\_2] [complex (2)]. Combining the techniques of nickel *K*- and sulfur *K*-edge X-ray absorption spectroscopy with high-resolution X-ray charge density modeling, together with theoretical calculations, the actual oxidation states of the central Ni atoms in these two complexes are investigated. Ni ions in two complexes are clearly in different oxidation states: the Ni ion of complex (1) is formally Ni<sup>II</sup>; that of complex (2) should be formally Ni<sup>III</sup>, yet it is best described as a combination of Ni<sup>2+</sup> and Ni<sup>3+</sup>, due to the involvement of the non-innocent ligand in the Ni–*L* bond. A detailed description of Ni–S bond character ( $\sigma$ , $\pi$ ) is presented.

## 1. Introduction

In the last few decades, metal dithiolene complexes have attracted continuous interest due to their wide application in many catalytic reactions (Ahmadi *et al.*, 2018) and bioinor-ganic electron transfer media (Wang & Stiefel, 2001), and their magnetic (Vieira *et al.*, 2015) and linear or nonlinear optical (Espa *et al.*, 2018) properties. Dithiolenes are non-innocent ligands (Fig. 1; Chuang *et al.*, 2017) that can affect the electronic structure of their complexes by providing the central metal with electron density shifted from the sulfur *p*-orbital









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# quantum crystallography

Table 1Experimental details.

	Complex (1) at 100 K	Complex (2) at 100 K	Complex (2) at 15 K
Crystal data			
Chemical formula	(MePh <sub>3</sub> P) <sub>2</sub> [Ni <sup>II</sup> (bdtCl <sub>2</sub> ) <sub>2</sub> ]- 2(CH <sub>3</sub> ) <sub>2</sub> SO	$(MePh_3P)[Ni^{III}(bdtCl_2)_2]$	$(MePh_3P)[Ni^{III}(bdtCl_2)_2]$
$M_{ m r}$	1187.76	754.20	754.20
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	100.0 (1)	100.0 (1)	15.0 (4)
a, b, c (Å)	13.8788 (1), 11.5765 (1), 16.4387 (1)	13.3664 (1), 14.4849 (1), 15.9712 (1)	13.3785 (1), 14.4463 (2), 15.9474 (2)
$\beta$ (°)	90.651 (1)	93.054 (1)	93.364 (1)
$V(\dot{A}^3)$	2641.00 (3)	3087.81 (4)	3076.84 (6)
Z	2	4	4
Radiation type, wavelength (A)	Ag $K\alpha$ , $\lambda = 0.56083$	Ag $K\alpha$ , $\lambda = 0.56083$	Synchrotron, $\lambda = 0.30996$
$\mu (\text{mm}^{-1})$	0.47	0.68	1.33
$D_{\rm x} (\rm g \ cm^{-3})$			
Scan type	$\omega$ scans	$\omega$ scans	$\omega$ scans
Crystal size (mm)	$0.32 \times 0.18 \times 0.05$	$0.23 \times 0.16 \times 0.03$	$0.09 \times 0.05 \times 0.03$
Data collection			
Diffractometer	Stoe Stadivari	Stoe Stadivari	Bruker D8 goniometer
Absorption correction	Integration (X-RED32; Stoe & Cie, 1997)	Integration (X-RED32; Stoe & Cie, 1997)	Multi-scan ( <i>SADABS2014/5</i> ; Bruker, 2015)
$T_{\min}, T_{\max}$	0.934, 0.985	0.262, 0.834	0.894, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	423 226, 32 089, 21 588	653 883, 36 081, 25 847	831 499, 89 538, 64 088
R <sub>int</sub>	0.046	0.030	0.050
$(\sin \theta / \lambda)_{\rm max} ({\rm \AA}^{-1})$	1.142	1.126	1.514
SHELXL (IAM) refinement			
No. of independent reflections	32 089	36 081	88 732
$R_{\rm int}, R_{\sigma}$	0.0460, 0.0231	0.0303, 0.0134	0.0501, 0.0328
No. of data, restraints, parameters	32 089, 0, 316	36 081, 0, 374	88732, 0, 374
Goodness-of-fit on $F^2(S)$	1.00	1.03	1.03
Final R indexes $[I^2 > 2\sigma(I)]$	$R_1 = 0.0328, wR_2 = 0.0841$	$R_1 = 0.0263, wR_2 = 0.0670$	$R_1 = 0.0319, wR_2 = 0.0782$
Final R indexes (all data)	$R_1 = 0.0651, wR_2 = 0.0983$	$R_1 = 0.0263, wR_2 = 0.0670$	$R_1 = 0.0550, wR_2 = 0.0845$
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min} \ ({ m e} \ { m \AA}^{-3})$	1.14, -0.76	0.83, -0.74	2.47, -3.18
Multipole refinement on $F^2$			
R(F), wR(F), GOOF(S)	0.0276, 0.0236, 1.2062	0.0231, 0.0249, 1.0618	0.0262, 0.0281, 1.1794
$R(F^2)$ , $wR(F^2)$ , GOOFw	0.0360, 0.0464, 3.1166	0.0265, 0.0251, 2.6217	0.0354, 0.0544, 1.6107
$N_{\rm ref}/N_{\rm v}$ (observed reflections/para-	217.9840	326.5168	53.5813
meters)			
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$	1.34, -0.67	1.36, -1.68	1.46, -3.03

Computer programs: SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), OLEX2 (Dolomanov et al., 2009).

bearing an occupied lone pair to an empty/depopulated metal *d*-orbital (Sugimoto *et al.*, 2009). Hence, because of a charge share between the metal center and the sulfur atoms of di-thiolenes, the oxidation state of the central metal atom becomes unresolved. Knowledge of the detailed electronic structure can be correlated with the compound redox properties in order to assess the formal oxidation state, as shown by Machata *et al.* (2014). Thus, a detailed characterization of the oxidation state of the central metal atom, and a clear description of the metal–ligand non-innocent interactions, can be used in material design to understand and predict the structure–property relationship.

Metal complexes of 'non-innocent' ligands (Jørgensen, 1966*a*) can exist either as metal–ligand radicals  $M^{q+}(L^{\bullet})$  or as higher valent metal complexes  $M^{(q+1)+}(L^{-})$ . The redox site within the complex can be significantly changed by fine electronic structure changes (Asami *et al.*, 2012). Typically, complexes containing the 'non-innocent' ligands are redox active at low potentials.

The formal oxidation state of an atom is defined (Karen *et al.*, 2016) as its charge after ionic approximation of its heteronuclear bonds. Unfortunately, this IUPAC definition cannot account for differences in the local chemical environment (Gimferrer *et al.*, 2020) and the formal oxidation state often differs from the value obtained by different physico-chemical methods (Shimazaki *et al.*, 2007).

The oxidation states of transition metals in complexes can be defined in terms of their *d*-electron configurations,  $d^n$ , as physical (or spectroscopic) oxidation states (Jørgensen, 1966b). For the (innocent) tetrachlorocomplexes of the first row of transition metals at various levels of theory (Štekláč & Breza, 2021) it has been shown that changes of the physical oxidation states during redox processes and of the corresponding *d*-electron populations at the central atom are practically equal.

There are several ways in which the oxidation state of central atoms in coordination compounds can be determined experimentally. On the basis of their stoichiometry and assuming that the cations and anions have integer charge and the intercalated solvent is neutral, the content of the whole unit cell should be electroneutral. Experimental techniques for the oxidation states assessment are based on diverse properties of the system studied. Electron spin resonance (ESR) measurement (Goldfarb & Stoll, 2017) easily distinguishes between ESR silent (all electrons are paired) and ESR active (there are unpaired electrons) systems. X-ray absorption spectroscopy is sensitive to absorption of primary X-ray beams close to the absorption edge (Chuang *et al.*, 2017). The Ni–S distances obtained from the X-ray crystal structures could also distinguish between the Ni<sup>2+</sup> and Ni<sup>3+</sup> oxidation states of the central atom (Sellmann *et al.*, 2000).

The main aim of this study is to assess the differences in the electron density distribution of the central metal atom and the non-innocent ligand in coordination compounds with a formal charge of the central nickel atom of +2 and +3. Furthermore, we explore the effects of the metal-ligand interactions that may cause the redistribution of the electron density and account for the removal of the quasi-symmetry of the ligand.

## 2. Experimental

## 2.1. Data collection and processing

The preparation of both complexes is described in supporting information (Section S1). A suitable recrystallized sample of bis(methyltriphenylphosphonium) bis(3,6-dichlorobenzene-1,2-dithiolato- $\kappa^2 S, S'$ )-nickel(II) bis(dimethyl sulfoxide) solvate [complex (1)] and methyltriphenylphosphonium bis(3,6-dichlorobenzene-1,2-dithiolato- $\kappa^2 S, S'$ )nickel(III) [complex (2)] were used for single-crystal highresolution X-ray diffraction experiments. Data collection (Table 1) is described in supporting information (Section S2).



Figure 2

Local coordinate system of the nickel atom(s) in (a) (1) and (b) (2). Symmetry codes: (A) -x, 2 -y, 1 - z; (B) 1 - x, 1 - y, 2 - z; (C) -x, 1 - y, 1 - z.

#### 2.2. Multipole model refinements

Starting atom coordinates and atom displacement parameters were taken from a routine *SHELXL* (Sheldrick, 2015) refinement and all other refinements were carried out on  $F^2$ using the *XD2015* (Volkov *et al.*, 2015) suite of programs. Furthermore, the determination of the atomic basins defined within the framework of the Quantum Theory of Atoms in Molecules (QTAIM) (Bader *et al.*, 1979, 1981; Bader, 1990) and the integration of atomic properties within their QTAIM basins were performed using the *TOPINT* option in the inhouse version of the *XDPROP* module of the software package *XD2015* (Volkov *et al.*, 2015). Both the default and the local version of *XDPROP* (*XDPROP*<sup>local</sup>) were used. The *XDPROP*<sup>local</sup> code is described in supporting information (Section S3).

Our refinement strategy was the same as described in our previous studies (Kožíšek et al., 2002; Herich et al., 2018; Adamko Koziskova et al., 2021), including the use of the relativistic Su and Coppens wavefunctions (Su & Coppens, 1998). For each compound, two multipole refinements were performed that employed different nickel wavefunctions that described the spherical core and valence, and the aspherical deformation density of the metal atom: (a) the neutral Ni atom ([Ar]  $4s^2 3d^8$ ) and (b) the positive cation Ni<sup>2+</sup> ([Ar]  $4s^0$  $3d^8$ ) wavefunction. For complex (2) at 15 K, the positive cation  $Ni^{3+}$  ([Ar]  $4s^0 3d^7$ ) wavefunction was also used. For simplicity, we shall call them the neutral nickel (Ni<sup>0</sup>), Ni<sup>2+</sup> and Ni<sup>3+</sup> scattering curves. In the case of the Ni<sup>2+</sup> scattering curve, the two electrons removed from the nickel atom were evenly distributed at the beginning of the refinement among the four ligand S atoms. In the following, we will focus foremost on the multipole refinement using the Ni<sup>2+</sup> cation scattering curve; results of the neutral scattering curve are summarized in Table S1. In kappa (contraction-expansion parameter) and in unrestricted refinements, the charges on cations, anions and

> the neutral solvent molecule in the case of complex (1), as well as the charges on cations and anions for structure (2) were kept constant. The local coordinate system was chosen to be the same as in the paper by Chuang et al. (2017), the z-axis is perpendicular to the molecule plane and the x, y vectors are at bi-sections of two neighboring S-M-S angles (as shown in Fig. 2). Due to variations of the scale factor, we have introduced 20 scale factors into the multipole refinement, one for each group, as was suggested by Niepötter et al. (2015). Hexadecapoles for Ni and S, octapoles for C, N, [O in complex (1)], and dipoles for H are used in the multipole model. Constraints due to local symmetry were used for nickel atoms. Chemical constraint was not used. For complex (1), the sulfur atom of the solvent has a different kappa value from the sulfur

atoms of the dithiolene ligand, while kappa primes were not refined. As the symmetry-equivalent data were collected with different TBAR (the path of the primary and diffracted beam in the crystal) values, all non-averaged data were used in the refinements. We also attempted to apply the anisotropic secondary extinction correction (Herich *et al.*, 2018), but in both crystal structures, this correction was found unnecessary. The coordination polyhedra in both compounds are equal; the nickel atom is in a special position, thus one half of the coordination polyhedron is an independent part.

#### 2.3. Theoretical calculations

In vacuo single-point calculations and geometry optimizations have been performed using the Gaussian16 (Frisch et al., 2016) program suite employing the B3LYP/def2-TZVP (Becke, 1993; Lee et al., 1988; Becke, 1988; Weigend & Ahlrichs, 2005) computational protocol. Localized orbitals and their Mulliken atomic population analysis (MPA) were obtained via ORCA4.2.0 package (Neese, 2012, 2017). The exploration of the topology of electron density utilized the Quantum Theory of Atoms in Molecules (OTAIM) analysis (Bader, 1990) using the AIMAll package (Keith, 2019) and Gaussian16 fchk files. The periodic calculations were made using the CRYSTAL17 package (Dovesi et al., 2017, 2018) and the POB-DZVP basis set with TOPOND being used for the QTAIM analysis (Gatti et al., 1994; Peintinger et al., 2013). In addition, the *d*-character and bonding mode analysis of the central atom has been made with the help of the domainaveraged Fermi holes (DAFHs) approach using the DGrid5.1 package (Kohout, 2019) and the Gaussian16 fchk files. The Molekel package (Flükiger et al., 2002) has been used for the visualization of molecular orbitals and DAFH eigenvectors.



Figure 3

ORTEP plots of the asymmetric units of (a) complex (1) and (b) complex (2). Displacement ellipsoids are drawn at the 30% probability level.

## Table 2

Selected experimental bond lengths (Å) and angles (°) from multipole refinements (Ni<sup>2+</sup> scattering curve).

Complex	T (K)	Ni-S	S-C	C-C	∠ S–Ni–S
(1)	100	2.17338 (6)	1.7443 (3)	1.4162 (4)	91.333 (2)
~ /		2.17009 (5)	1.7411 (3)	( )	( )
(2)	100	2.14898 (4)	1.7305 (2)	1.4042 (3)	92.7829 (16)
		2.13685 (4)	1.7279 (2)		
		2.14239 (4)	1.7350 (2)		92.3613 (15)
		2.14688 (4)	1.7362 (2)		
(2)	15	2.15856 (6)	1.7339 (2)	1.4102 (3)	92.813 (2)
		2.14107 (6)	1.7366 (2)		
		2.14621 (6)	1.7436 (2)	1.4119 (3)	92.216 (2)
		2.15556 (6)	1.7409 (2)		

Nickel K-edge and sulfur K-edge X-ray absorption transitions (Rees et al., 2016; Maganas et al., 2016; Kowalska et al., 2016) have been calculated in the ORCA4.2.0 package using the ZORA Hamiltonian (van Lenthe et al., 1993; van Wüllen et al., 1998) at the B3LYP/ZORA-Def2-TZVP level of theory, with the autoaux option activated and 25 transitions accounted for in the TD-DFT calculation. Theoretical twodimensional (Laplacian and deformation density) maps, with a focus on a direct comparison of the B3LYP/6-311G\* (Krishnan et al., 1980; McLean & Chandler, 1980; Wachters et al., 1970) electron density with the experimentally derived charge density, have been utilized in the Tonto package (Jayatilaka & Grimwood, 2003).

## 2.4. X-ray absorption spectroscopy

Nickel *K*-edge X-ray absorption spectra measurements were carried out at the beamline BL17C at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Ni samples were evenly spread on the Kapton tape. The XAS measurements were performed in fluorescence mode using a Lytle detector, the intensity of incident beam and the reference spectra of the Ni metal foil were monitored by ion chambers for normalization and energy calibration (8333 eV).

Sulfur *K*-edge X-ray absorption experiments were taken at beamline BL16A of NSRRC (Taiwan). The samples were ground and dispersed on Mylar tape to avoid any fluorescence saturation and self-absorption. Spectra were measured in fluorescence mode utilizing a Lytle detector, and the sample chamber was filled with high-purity He gas to avoid air absorption. The photon energy was calibrated at 2472.02 eV with the peak at the first pre-edge of  $Na_2S_2O_3$ ·5H<sub>2</sub>O (Rose *et al.*, 1998).

## 3. Results and discussion

3.1. Structural features and results of the multipole refinement

Both transition metal anions in the studied compounds are isostructural and have a planar geometry in a formal  $D_{2h}$ symmetry when considering the NiS<sub>4</sub> coordination polyhedron. In both compounds, the nickel atoms are in the center of symmetry. In complex (1), the independent part of the unit

#### Table 3

Results of multipolar refinement using the positive scattering curve  $Ni^{2+}$  ([Ar]  $4s^0 3d^8$ ).

Individual *d*-orbital populations,  $\Sigma$  is their sum (DFT 4*s*-like orbital population in parentheses), GROUPS is the charge of particular cation, anion/anions and the neutral molecule. *M*1(Ni) is the monopole population of Ni, *Q* is the QTAIM charge of Ni and V001 is the volume (Å<sup>3</sup>) of the atomic basin of Ni. *R*-factor is defined here as  $R(F^2)$  (%) for observed data.

Compound	Monopoles (start)	GROUPS	$d_{z2}$ $d_{xz}$	$d_{yz} \ d_{x2-y2}$	$d_{xy} \Sigma(\mathbf{S}_{\sigma})$	$\begin{array}{l} M1(\mathrm{Ni})\\ [\mathrm{NiS}_4\mathrm{C}_{12}\mathrm{Cl}_4\mathrm{H}_4] \end{array}$	Q (Ni)	V001 (Ni) <i>R</i> -factor
(1) at 100 K	Ni = 4, S = 7 P = 4	G1 = -1, G2 = -2 G3 = +1, G4 = 0	2.11	1.97 1.92	0.90 8.87	4.4327 -1.78	+0.933	14.33 2.7605
(1) DFT in vacuo	<b>I</b> = 1	05 - 11, 01 - 0	1.930 1.967	1.92 1.934 1.900	1.156, 8.787 (0.643)	1.70	+0.525	15.7
(2) at 100 K	Ni = 4, S = 6.75 P = 4	$G1 = -2, G2 = -\frac{3}{2}$ $G3 = -\frac{3}{2}, G4 = +1$	2.08, 1.94 1.52, 1.94	2.04, 1.65 1.66, 1.53	0.74, 1.02 8.04, 8.07	4.0216, 4.0361 -0.66, -0.78	+1.706, +1.679	13.21, 13.19 2.2897
(2) DFT in vacuo charge		2, 2, 2, 1	1.958	1.965	1.231	,		15.2
(2) DFT in vacuo spin			1.625 0.005 0.367	1.919 0.002 0.012	8.698 (0.655) 0.053 0.439 (0.002)		+0.619	
(2) at 15 K	Ni = 4, S = 6.75, P = 4	$G1 = -2, G2 = -\frac{3}{2}$ $G3 = -\frac{3}{2}, G4 = +1$	1.73, 2.02 1.59, 1.56	1.82, 1.84 1.95, 1.85	1.03, 0.75 8.12, 8.02	4.0585, 4.0105 -0.76, -0.78	+1.665, +1.761	12.485 , 12.395 2.6157

Table 4

Charges of atoms in the  $[NiL_2]^{q^-}$  anion for  $[Ni^{x+}S_4C_{12}Cl_4H_4]^{x-4}$ : (PPh<sub>3</sub>CH<sub>3</sub>)<sup>+</sup> ratios of 1:2 and 1:1 for (1) and (2), respectively (Ni<sup>2+</sup> scattering curve).

DFT spi	n populations	are given i	in parentheses.
		<i>u</i>	

			~	<i>a</i> (		~	<b>a</b> 14	~	***	~		~	<b>C11</b>		
Compound/Atom	Nil Ni2	S1 S3	C1 C7	C6 C12	S2 S4	C2 C8	Cl3	C3 C9	H3 H9	C4 C10	H4 H10	C5 C11	Cl2 Cl4	$L^{q-}$	$[NiL_2]^{q-1}$
(1) 100 K, <i>XDPROP</i>	0.93	-0.11	-0.08	-0.13	-0.24	-0.02	-0.00	0.03	-0.03	0.22	-0.52	-0.03	-0.44	-1.35	-1.77
(1) 100 K, XDPROP <sup>local</sup>	0.744	-0.086	-0.085	-0.125	-0.211	0.000	0.012	0.030	-0.037	0.224	-0.520	-0.019	-0.416	-1.233	-1.722
(1) in vacuo, AIMAll	0.525	-0.210	-0.136	-0.133	-0.208	0.048	-0.313	-0.032	0.001	-0.031	0.003	0.059	-0.311	-1.263	-2
(1) periodic, TOPOND	0.444	-0.116	-0.276	-0.277	-0.177	0.023	-0.231	0.328	0.043	0.029	0.044	0.004	-0.251	-0.856	-1.268
(2) 100 K, <i>XDPROP</i>	1.71 1.68	$-0.30 \\ -0.21$	$-0.14 \\ -0.19$	$-0.19 \\ -0.19$	$-0.26 \\ -0.09$	$0.07 \\ -0.03$	$-0.24 \\ -0.26$	$0.07 \\ 0.00$	$0.04 \\ -0.04$	$-0.10 \\ -0.05$	0.08 0.02	$0.04 \\ 0.01$	$-0.24 \\ -0.20$	-1.17 -1.23	$-0.63 \\ -0.78$
(2) 100 K, XDPROP <sup>local</sup>	1.448 1.454	$-0.289 \\ -0.186$	$-0.136 \\ -0.169$	$-0.185 \\ -0.185$	$-0.256 \\ -0.050$	$0.066 \\ -0.169$	$-0.248 \\ -0.253$	$0.070 \\ 0.002$	$0.036 \\ -0.053$	$-0.097 \\ -0.046$	0.063 0.008	0.038 0.032	$-0.246 \\ -0.192$	-1.184 -1.261	$-0.920 \\ -1.068$
(2) in vacuo, AIMAll (spin)	0.619 (0.465)	-0.126 (0.104)	-0.128 (0.005)	-0.125 (0.004)	-0.123 (0.108)	0.069 (0.012)	-0.262 (0.000)	-0.008 (0.011)	0.038 (0.000)	-0.007 (0.010)	0.041 (0.000)	0.079 (0.013)	-0.259 (0.000)	-0.810	-1
(2) periodic, TOPOND	0.499 0.506	-0.033	-0.299	-0.337	-0.078	0.004	-0.233	0.270	0.031	0.043	0.060	0.055	-0.162	-0.678	-0.858
(2) 15 K, XDPROP	1.66 1.76	$-0.11 \\ -0.07$	$-0.06 \\ -0.04$	$-0.26 \\ -0.11$	0.09 0.02	$0.01 \\ -0.15$	$-0.26 \\ -0.20$	$-0.54 \\ 0.10$	$0.06 \\ -0.23$	$0.04 \\ -0.13$	$-0.10 \\ -0.09$	$0.13 \\ -0.01$	$-0.18 \\ -0.35$	$-1.16 \\ -1.28$	$-0.66 \\ -0.80$

cell is one half of the  $[NiL_2]^{2-}$  anion, in complex (2) there are two independent coordination polyhedra, with one half of each being independent due to the inversion Ni centre. The central nickel atom is coordinated by four sulfur donor atoms from two bdtCl<sub>2</sub> ligands (Fig. 3). The only difference between complexes (1) and (2) is the ratio  $[Ni^{x+}S_4C_{12}Cl_4H_4]^{x-4}$ : (PPh<sub>3</sub>CH<sub>3</sub>)<sup>+</sup>. For (1) (Ni<sup>II</sup>, x = 2) the ratio is  $[NiS_4C_{12}Cl_4H_4]^{2-}$ : (PPh<sub>3</sub>CH<sub>3</sub>)<sup>+</sup> = 1:2 ( $\frac{1}{2}$ :1) and for (2) (Ni<sup>III</sup>, x = 3) the ratio is  $[NiS_4C_{12}Cl_4H_4]^{-}$ : (PPh<sub>3</sub>CH<sub>3</sub>)<sup>+</sup> = 1:1 ( $\frac{1}{2}$ +  $\frac{1}{2}$ :1). In the crystal structure of complex (1), a neutral dimethylsulfoxide solvent is also present.

The main geometrical differences between the two compounds are in the interatomic Ni-S distances [in complex (1): 2.16874(5)-2.17543(6) Å; in complex (2):

2.13677 (4)–2.15856 (6) Å] and S–Ni–S angles [in complex (1): 91.350 (2)–91.333 (2) $^{\circ}$ ; in complex (2): 92.7808 (16)-92.813 (2)°] (see Tables 2 and S2). It is interesting to note that the interatomic bond distances Ni-S in complex (1) from the multipolar refinements using the  $Ni^0$  and  $Ni^{2+}$  scattering curves differ from each other by more than  $20\sigma$ (although the  $\sigma$  values are rather small and the shift is less than 0.002 Å), while for complex (2) for both data (100 K and synchrotron 15 K), the interatomic bond distances from the two refinements are essentially the same. The residual density shows only a few weak maxima around the heavy atoms due to inaccuracies of high-angle diffractions (see Fig. S1). In the following, we describe the features of the experimental electron density distribution in complexes (1) and (2) from the aspherical multipole model while comparing with the theoretical data. A rigorous comparison must be performed using the same concepts. As such, we shall consider (a) the atomic charges as defined within the framework of Bader's QTAIM (experimental ones were obtained by default and local *XDPROP* version, Table 4), (b) the electron densities and the Laplacians at the bond critical points (BCPs), (c) twodimensional maps of the deformation density and the Laplacian, and finally (d) the d-orbital populations and the oxidation state of the central Ni atoms.

(a) The analysis of the OTAIM-based atomic charges (Tables 3 and 4, and Table S1) shows the importance of the scattering curve choice (Ni<sup>2+</sup> [Ar]  $4s^0 3d^8$  and Ni<sup>0</sup> [Ar]  $4s^2 3d^8$ ) and the integration accuracy (default XDPROP versus  $XDPROP^{local}$ ). It is found that Ni<sup> $\hat{II}$ </sup> in complex (1) has a lower charge than Ni<sup>III</sup> in complexes (2) at 100 K and 15 K. The closest agreement between experimental and DFT charges of Ni is obtained for the Ni<sup>0</sup> [Ar]  $4s^2 3d^8$  scattering curve integrated with XDPROP<sup>local</sup>, see Tables S1 and S3a. It is interesting to note that while the DFT QTAIM-based Ni charges in (1) and (2) are within 0.1 electrons (e) of each other (charges are between 0.5–0.6 e) (see Tables 3 and 4), the experimental QTAIM charges show a *ca* doubled difference: 0.7–0.8 e in (1) versus (2) when using the Ni<sup>2+</sup> scattering curve, and 0.2–0.4 e in (1) versus (2) when using the  $Ni^0$  scattering curve, see Tables 3 and 4, and Table S1. In general, we observe a significant reduction (by 0.9-1.4 e) in the OTAIM charge of the nickel atom when switching from the Ni<sup>2+</sup> scattering curve to that of Ni<sup>0</sup>, see Table S1. Averaging all charges for anions  $[Ni(bdtCl_2)_2]^{q-}$  gives the charge of q = -2.06 for (1) and q =-1.01 for (2), see Table S1. These q values of the anion  $[NiL_2]^{q-}$  are close to -2 and -1 for (1) and (2), respectively, as assumed by stoichiometry (see Tables 3 and 4, and Table S1). It is fair to note that in the DFT results, when accounting for the presence of the cation (either in the in vacuo or periodic calculations), a charge transfer of  $\sim 0.75$  e is found for (1). Furthermore, the overall ligand charges also do not change dramatically when comparing (1) and (2), *i.e.* by less than 10%, pointing towards the delocalized oxidation locus and the non-innocent scenario in (2), see Tables 3 and 4, and Table S1.

In this case the Ni<sup>2+</sup> scattering curve volumes match with the DFT results, while for the Ni<sup>0</sup> scattering curve the *XDPROP*<sup>local</sup> version leads to a closer agreement with the DFT prediction, see Table 3 and Table S1. The diffuse  $4s^2$ orbital, which is populated for the neutral scattering curve, needs a fine tuning of the integration protocol as provided in *XDPROP*<sup>local</sup>.

Let us further emphasize that in coordination compounds, the central atom never has the same positive charge as the formal oxidation state, but the positive charge is always smaller due to dative interactions (Herich *et al.*, 2018; Scatena *et al.*, 2020; Adamko Kožíšková *et al.*, 2021). Furthermore, ESR measurements have clearly confirmed that system (1) is ESR silent unlike (2), which contains an unpaired electron (Machata *et al.*, 2014) as also reported for similar species (Chuang, 2017).

### Table 5

Topological properties associated with bond critical points of the Ni-S and S-C bonds in Ni complexes.

 $R_{ij}$  is the bond path length,  $d_1$  is first atom to the BCP distance,  $\rho_c$  is BCP electron density and  $\nabla^2 \rho_c$  is BCP Laplacian (Ni<sup>2+</sup> scattering curve).

		$R_{ij}$	$d_1$	$ ho_{\rm c}$	$\nabla^2  ho_{ m c}$
Bond	Complex	(Å)	(Å)	$(e Å^{-3})$	$(e Å^{-5})$
Ni-S	(1)	2.174	0.984	0.466 (3)	8.573 (3)
		2.171	0.992	0.526(2)	8.390 (2)
Ni-S	(2)	2.151	0.964	0.528 (2)	9.097 (2)
		2.137	0.958	0.535 (2)	9.349 (2)
		2.147	0.964	0.529 (2)	8.881 (2)
		2.148	0.981	0.577 (2)	8.566 (2)
Ni-S	(2) at 15 K	2.160	0.982	0.461 (7)	8.549 (4)
		2.143	0.971	0.494 (7)	9.003 (5)
		2.149	0.959	0.435 (7)	9.058 (4)
		2.156	0.970	0.501 (6)	9.174 (4)
S-C	(1)	1.745	0.925	1.289 (8)	-3.83(2)
		1.741	0.713	1.346 (7)	-4.18(2)
S-C	(2)	1.731	0.922	1.397 (5)	-5.52(1)
		1.728	0.920	1.428 (5)	-5.58(1)
		1.735	0.925	1.413 (5)	-5.69(1)
		1.736	0.888	1.384 (5)	-5.84(1)
S-C	(2) at 15 K	1.735	0.921	1.42 (2)	-4.81(4)
		1.738	0.893	1.32(2)	-3.10(4)
		1.744	0.941	1.44 (2)	-4.31 (4)
		1.742	0.892	1.31 (2)	-4.42(4)

(b) The experimental BCP electron densities for Ni-S, as well as S-C bonds are slightly lower in complex (1) compared to complex (2) for the 100 K data, see Table 5. The same trend is observed for the BCP Laplacians. Furthermore, it can be seen that the Ni-S and S-C BCP electron densities and Laplacians in (2) are usually smaller in magnitudes in the 15 K data as compared to the 100 K results. The theoretical DFTbased BCP characteristics are compiled in Table S3, and qualitatively follow the experimental findings, although the Ni-S BCP electron density is higher by about 0.2 e  $Å^{-3}$  $(0.64-0.67 \text{ e} \text{ Å}^{-3} \text{ versus } 0.47-0.53 \text{ e} \text{ Å}^{-3})$  and the DFT Laplacians are nearly half compared to the experimental values (4.4–4.8 e  $Å^{-5}$  versus 8.4–9.3 e  $Å^{-5}$ ). For S–C bonds, the experimental and theoretical electron densities at BCPs are close to each other (1.3–1.4 e  $Å^{-3}$ ), but the DFT Laplacians are about two to three times larger in magnitudes than the experimental ones (-10.4 to  $-10.6 \text{ e} \text{ Å}^{-5}$  versus -3.1 to  $-5.7 \text{ e} \text{ Å}^{-5}$ ). That is, the experiment and theory always agree in the sign of the Laplacian at the Ni-S and S-C BCPs.

(c) As can be seen from Figs. 4 and Tables 3 and 4 (the results of the Ni<sup>2+</sup> scattering curve), the electron density distributions for the Ni<sup>II</sup> complex (1) and Ni<sup>III</sup> complex (2) atoms are quite similar. The experimental deformation density (DD) maps in the molecular plane, as displayed in Figs. 4(*a*) and 4(*b*), provide additional insight into the metal-ligand bonding character in the studied complexes. It is worthwhile to mention that the density distribution of the Ni atom in the DD maps can be compared to a spherical Ni  $d^8$  density with 1.6 e equally distributed in the five 3*d* orbitals. The donor–acceptor (dative) interaction is mediated via the  $p_{\sigma}(S)-d_{xy}(Ni)$  orbitals (see red dashed regions at Ni in Figs. 4(*a*) and 4(*b*). Naturally, this region is in negative (red dashed) contours when a spherically averaged Ni atom with  $d_{xy}$  population of 1.6 e is

subtracted from  $d_{xy}$  orbital populations below (around) 1 e. Furthermore, one can see the unequal character of the Ni-S dative bonds of (1), *i.e.* the different bond lengths are manifested in the different BCP characteristics, as well as in the different shapes of the red dashed regions of the DD map of (1). On the other hand, the blue solid regions of Ni highlight the  $d_{x2-y2}$  density distribution (population). The larger orbital population  $d_{x2-y2}$  in (1) compared to (2) is manifested by a larger blue region.

The lone electron pairs of the sulfur atoms S1 and S2 are somewhat more pronounced in (1) than in (2) [see Figs. 4(*a*) and 4(*b*)]. Interestingly, the Laplacian maps for (1) and (2) are fairly similar [Figs. 4(*c*) and 4(*d*)]. In the case of the theoretical DFT-based deformation density, both the (1) and (2) maps confirm the S-to-d<sub>xy</sub>(Ni) donor–acceptor interaction, see Figs. S2(*b*) and S2(*d*), and the differences between (1) and (2) in the Ni-atom region are much less pronounced than in the experiment.

(d) According to the chosen local coordinate system, the orbitals  $d_{z2}$ ,  $d_{xz}$ ,  $d_{yz}$  and  $d_{x2-y2}$  have their electron density populations close to the fully occupied orbitals in complex (1), while the 'depopulated'  $d_{xy}$  orbital is occupied by 0.9 electrons. The  $d_{xy}$  orbital of the Ni atom acts as an electron acceptor with the sulfur atom of the bdtCl<sub>2</sub> ligand being an electron donor. In (1), there is good agreement for the *d*-orbital populations between experiment and theory (Table 3), and one can assign a formal oxidation state of II to the central Ni atom of (1).



#### Figure 4

Experimental (100 K) static electron deformation density in the plane defined by the atoms Ni1–S1–S2 in (*a*) complex (1) and (*b*) complex (2). The contour spacing is 0.1 e Å<sup>-3</sup>, with positive contours drawn with solid blue lines, negative contours with dashed red lines and zero values with black dotted lines. The experimental (100 K) distribution of the Laplacian in the Ni1–S1–S2 plane of (*c*) complex (1) and (*d*) complex (1). The contours are drawn at  $-1.0 \times 10^{-3}, \pm 2.0 \times 10^{n}, \pm 4.0 \times 10^{n}, \pm 8.0 \times 10^{n}$  (n = -3, -2 - 1, 0, +1, +2 + 3) e Å<sup>-5</sup> and zero values.

(Here the Ni<sup>0</sup> scattering curve yields lower *d* populations for the 'fully' occupied *d*-orbitals, around 1.85, which has to be assigned to the presence of the  $4s^2$  electron density, thus the total *d*-population is lower by 0.6 e compared to the Ni<sup>2+</sup> scattering curve, see Table S1). In the case of (2), the 15 K experiment results are close to the DFT predictions (Table 3), while for the 100 K data, we also observe a considerably lower electron population for the orbitals  $d_{yz}$  and  $d_{x2-y2}$  (1.5–1.6 e). When considering the agreement between the 15 K experiment and DFT, the 1.6 e populated  $d_{xz}$  orbital resembles a partial oxidation on Ni<sup>II</sup> with a strong non-innocent contribution of the ligands, leading to an intermediate II/III formal oxidation state of Ni in (2).

3.2. Theoretical results (Ni oxidation state and non-innocent interactions)

QTAIM atomic charges and spin populations as well as bond critical point (BCP) characteristics are compiled in Tables 3 and S3, respectively. The summary of *d*-populations and Ni *d*-like localized orbitals is compiled in Table 3.

As already mentioned, in contrast to the experimental results (see Tables 3 and 4), the QTAIM charge of Ni changes only slightly upon oxidation, but one can find a considerable amount of the spin population on Ni<sup>III</sup> of (2), see Tables 3 and 4. These results are in good agreement with the experimental ESR finding in Machata et al. (2014), where one unpaired electron was confirmed for (2), and the rhombic spectra showed that its spin density is partially localized on the sulfur donor atoms as well. This is consistent with the DFT B3LYP results which localize one half of the spin population in (2) on sulfurs. Such spin density distribution reflects the change of the oxidation state, but because the unpaired electron (spin population) is only up to one half localized on the Ni atom, its oxidation state appears to be a Ni<sup>II/III</sup> intermediate. From the perspective of oxidation state assignment, we will briefly deal with the DFT-based *d*-populations in more detail, although they have been already mentioned previously. According to



Frontier orbital energy diagrams of (1) and (2).

the *d*-populations reported in Table 3, the central Ni atom in complex (1) is in oxidation state II ( $d^8$  configuration) in agreement with the assumptions of the crystal field theory (CFT). The occupation of Ni *d*-orbitals in complex (1) agrees with the square planar geometry, with doubly occupied  $d_{xz}$ ,  $d_{yz}$ and  $d_{z2}$  orbitals, an almost doubly occupied  $d_{x2-y2}$  orbital and only partially (up to half) occupied  $d_{xy}$  orbital, which is involved in the  $\sigma$  coordination bonding mode. This is also found in the experiment. In complex (2), the  $4\alpha d$  AOs ( $d_{xz}$ ,  $d_{yz}$ ,  $d_{z2}$  and  $d_{x2-y2}$ ),  $3\beta d$  AOs ( $d_{z2}$ ,  $d_{yz}$  and  $d_{x2-y2}$ ) can be identified, while  $\beta d_{xz}$  has a population of 0.63. The last mentioned  $d_{xz}$  population is involved in  $\pi$  interactions with the ligand, as will be mentioned later with respect to DAFHs and frontier orbitals. Hence, this seems to be a Ni<sup>II/III</sup> oxidation state intermediate (a situation which can be easily assigned to the non-innocent character of the ligand in this bonding situation). Localized *d*-orbitals also favor the formal  $d^8$ configuration for complex (1)  $(4\alpha + 4\beta)$  and the  $d^7$  configuration for complex (2)  $(4\alpha + 3\beta)$ , with a strong  $\pi$  back donation interactions that can be explained as a non-innocent ligand situation, and/or NiS<sub>4</sub> interaction).

The strong  $\pi$  back donation interactions in complex (2) are also manifested in the frontier orbitals, see Figs. 5 and S7. Apparently, the strong and antibonding  $\pi$  character in  $\beta$ -LUMO of (2) reflects the intermediate Ni<sup>II</sup>/<sup>III</sup> oxidation state feature. Furthermore,  $\beta$ -LUMO of (2) agrees totally with HOMO of (1). Therefore, in this orbital picture, one electron has been removed from an antibonding  $\pi$  HOMO of (1), thus complex (2) should have a stronger  $\pi$  interaction between S and Ni; that is, the oxidation occurs both at Ni and the ligand.

Domain-averaged Fermi holes (DAFH) analysis fully supports the conclusions made upon the MPA *d*-populations, localized orbitals and MO inspection. Ni in (1) is in the formal oxidation state II, and there is only a  $\sigma$ -coordination bonding mode, see Fig. S3 (DAFH eigenvectors with eigenvalues below 0.2 are shown in Fig. S7). In contrast, DAFH eigenvectors of (2) show only a slightly stronger  $\sigma$  interaction than (1) (when summing up the pictorially inspected eigenvalues), but there is the  $\pi$ -like interaction (see Fig. S3) with the eigenvalue (Ni domain occupation number) of 0.57 and the *d*-localized DAFH eigenvectors correspond to a formal  $d^7$  configuration.

### 3.3. X-ray absorption near-edge spectra

The nickel K-edge X-ray absorption near-edge spectra (XANES) of two Ni complexes, (1) and (2), have been measured (the normalized spectra are displayed in Fig. 6) with edge energies around 8336 and 8337 eV, respectively. Apparently, the edge energy of (2) is by 1.0 eV higher than that of (1). Although the absorption edge energy does provide information on the oxidation state of the metal ion, it is often affected by other factors, e.g. the coordination environment, the anion effect, etc. To compare some anionic Ni complexes with similar coordination spheres, XANES of these complexes together with that of Ni foil are depicted in Fig. 6, where the Ni oxidation states were discussed (Chuang et al., 2017; Hsieh et al., 2003; Lim et al., 2001). To further investigate whether the ligand plays any role in the oxidation-reduction processes of these complexes, sulfur K-edge XANES were explored, where the S-Ni bonding was manifested in the pre-edge region due to differences in the Ni 3d- and S p-character admixture of (Chuang et al., 2017: Sarangi et al., 2007: Szilagyi et al., 2003: Solomon et al., 2005). Normalized sulfur K-edge spectra of (1) and (2) are shown in Fig. 7, together with two other Ni complexes,  $(PyH)_{z}[Ni(S_{2}C_{2}(CN)_{2})_{2}]^{z}$ , z = 2 [complex (3)] and z = 1 [complex (4)] (PyH is C<sub>5</sub>H<sub>5</sub>NH) (Chuang *et al.*, 2017) in a very similar coordination sphere. Based on the literature (Szilagyi et al., 2003; Solomon et al., 2005), the pre-edge is located at 2469-2472 eV and the rising edge is located at 2472-2475 eV of sulfur K-edge spectra for a series of square planar bis(dithiolene) complexes of Ni (Sarangi et al., 2007). To obtain the exact peak position, the first and second derivatives of the spectra were taken; the transition energies are listed in Table 6 where the pre-edge and the rising energies are within



Figure 6

Comparison of the nickel *K*-edge absorption spectra for complexes (1) and (2) with related Ni<sup>III</sup> complexes.



**Figure** 7 Sulfur *K*-edge absorption spectra of four Ni complexes studied.

Table 6	
Assignment of the sulfur K pre-edge absorption for four Ni	complexes
$(\sigma^*; \sigma^*)$ of the Ni-S bond and $\pi^*:\pi^*$ of the Ni-S bond).	

Complex	Pre-edge energy (eV)	Assignment	Edge energy (eV)
$(3) (PvH)_2[Ni(S_2C_2(CN)_2)_2]$	2471.2	$1s \rightarrow \sigma^*$	2471.8
(4) $(PyH)[Ni(S_2C_2(CN)_2)_2]$	2470.1	$1s \rightarrow \pi^*$	2472.0
	2470.9	$1s \rightarrow \sigma^*$	
(1)	2471.4	$1s \rightarrow \sigma^*$	2472.3
(2)	2469.8	$1s \rightarrow \pi^*$	2472.6
	2470.8	$1s \rightarrow \sigma^*(\alpha)$	
	2471.4	$1s \rightarrow \sigma^*(\beta)$	

PyH is the pyridinium cation  $(C_5H_5NH^+)$ .

the range found in the literature. The transitions of the preedge absorption do give a great insight of the S—Ni bond characters: the transitions are assigned according to the frontier orbital descriptions based on theoretical calculations (Table S4). The theoretical assessment of the Ni and S *K*-edge transitions is summarized in Table S5, which lists the obtained transition energies, and Tables S6 and S7 that contain the excitation weights.

The shapes and energies of frontier orbitals are depicted in Fig. 5. Apparently, the pre-edge feature of (2) is more complicated than that of (1); so as in other two Ni complexes (4) and (3) (Chuang et al., 2017), since there is a singly occupied HOMO (SOMO) in both (2) and (4). The unpaired electron at the Ni site was confirmed in the literature (Maki et al., 1964) with the ESR signal. The pre-edge features of (1) and (3) have only one transition, signifying as S 1s to  $\sigma^*$  of S – Ni bond (LUMO); where those of (2) have three transitions, namely S 1s to  $\pi^*(\beta)$  and two  $\sigma^*(\alpha,\beta)$  of the S–Ni bond with a slight difference in energies. According to the nickel and sulfur K-edge XANES spectra, the difference between (1) and (2) must be associated with HOMO, which is mainly of a Ni-S $\pi^*$  character; it is fully occupied in (1), but only singly occupied in (2). This means that the electron density is delocalized between the Ni ion and the sulfur atoms of the non-innocent ligand through the  $\pi$  interaction. Due to the presence of Ni-S interactions, oxidation of (1) takes place on both the metal and the ligand sites. Therefore, this situation is best described in such a manner that the Ni ion in (2) contains admixtures of both Ni<sup>2+</sup> and Ni<sup>3+</sup> oxidation states (Chuang et al., 2017; Hsieh et al., 2003; Lim et al., 2001). Judging from the XANES, structural analysis, charge density work and theoretical calculations, Ni ions in two complexes are clearly in different oxidation states. The Ni ion of complex (1) is formally Ni<sup>II</sup>; the Ni ion of complex (2) should be formally Ni<sup>III</sup>, yet it contains a superposition of Ni<sup>II</sup> and Ni<sup>III</sup>.

## 4. Conclusions

The coordination mode in both complexes is similar and typical for square-planar coordination when the ligand donor atom interacts *via* its lone electron pair with the depopulated  $d_{xy}$  orbital of the central metal atom. It is found that the

multipole model (MM) charge density derived from the experimental data, especially the charge on the central atom, is sensitive to the choice of the scattering curve and proper integration settings. However, the trends clearly show that the charge on the central atom in (1) is less positive than in (2). Still, the MM-derived QTAIM charges, BCP characteristics and 2D maps, including *d*-populations, are found to be consistent with DFT. Although it is fair to note that the experimental charge of the entire  $[NiL_2]^{q-}$  anion is close to the charge corresponding to the stoichiometry, DFT finds the charge of the anion in (1) to be lower by 0.75 e. According to the DFT calculations, the QTAIM charges of the Ni atoms in (1) and (2) differ by only 0.1 e, while the experimental results show larger differences (from 0.35 to 0.80 e).

Considering the experimental MM *d*-populations and DFT B3LYP *d*-populations, frontier as well as localized orbitals, and last but not least the DAFH analysis, Ni in (1) is in the oxidation state II and in the case of (2) in an intermediate II/III state. When formally drawing a valid resonance structure of (2), half an electron is on Ni atom and the other on the sulfur atoms of the two ligands (Machata *et al.*, 2014), being a pure non-innocence example as found elsewhere (Chuang *et al.*, 2017).

XANES nickel and sulfur *K*-edge experiments and comparison with reference compounds confirm a higher percentage of Ni<sup>3+</sup> in (2) than in (1). In addition to the difference in the formal oxidation state difference in (1) and (2), the electron density distribution across the whole anion is affected manifesting the importance of  $\sigma$ ,  $\pi$ -bonding character of the S–Ni bonds.

In the experimental results we see two combined effects. One effect is that the positive charge on the central atom is always lower than the formal oxidation state, and the other, that one part of electrons is shifted from the central atom to the non-innocent ligand. Thus, the non-innocent ligand can adapt to the requirements of the central atom. As a ligand, it could be an anion  $L^{2-}$ ,  $L^{-}$  or neutral ligand L, or an intermediate between these three forms.

## 5. Related literature

The following references are cited in the supporting information: Ahrens *et al.* (2005); Ayachit (2015); Keith & Bader (1993); Lebedeb & Laikov (1999); Popeiler (1998); Press *et al.* (1992); Schreurs *et al.* (2010).

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