NJC

Cite this: *New J. Chem.*, 2011, **35**, 2179–2186

www.rsc.org/njc

PAPER

Antiferromagnetic ordering in cobalt(II) and nickel(II) 1D coordination polymers with the dithioamide of 1,3-benzenedicarboxylic acid†‡

Anton S. Lytvynenko,[a] Sergey V. Kolotilov,[ab] Olivier Cador,[b] Stéphane Golhen,[b] Lahcène Ouahab*[b] and Vitaly V. Pavlishchuk*[a]

Received (in Victoria, Australia) 27th February 2011, Accepted 3rd May 2011
DOI: 10.1039/c1nj20173e

A series of 1D coordination polymers $[Co(m\text{-}dtab)Cl_2]_n$ (**1**), $[Co(m\text{-}dtab)Br_2]_n$ (**2**) and $[Ni(m\text{-}dtab)_2(Br)_2]_n$ (**3**), where **m-dtab** = the dithioamide of 1,3-benzenedicarboxylic acid, were prepared. The structures of all complexes were determined by X-ray diffraction. Magnetic properties of the compounds were characterized by molecular susceptibility *vs.* T dependence in the temperature range from 2 to 300 K. All compounds possess antiferromagnetic exchange interactions, and antiferromagnetic ordering was found in $[Co(m\text{-}dtab)Br_2]_n$ and $[Ni(m\text{-}dtab)_2Br_2]_n$ at T_N = 2.9 K and 2.6 K, respectively. DFT calculations showed that exchange interactions in $[Co(m\text{-}dtab)(Hal)_2]_n$ could be transferred through two pathways: **m-dtab** between metal ions or interchain π–π stacking of aromatic rings, so the systems are not 1D from the viewpoint of magnetochemistry. The results of DFT calculations are consistent with the existence of magnetic ordering.

Introduction

Polynuclear complexes and coordination polymers are considered as the basis for creation of functional materials with non-trivial magnetic properties.[1] One of the important problems in this field of research is the development of ligands capable of transfering exchange interactions over long distances.[2] Several types of polynuclear systems containing paramagnetic centers bonded by long organic bridges were studied, such as, for example, a biphenyl bridge.[2f–j] It was found that transfer of exchange interactions over long distances is not a trivial case, and some ligands, despite the presence of alternating single and double bonds, even conjugated in some cases, do not transfer exchange interactions or lead to negligibly small coupling.[3] The studies of factors which influence the efficiency of exchange interactions transfer through long organic bridges is an actual task of coordination chemistry and material science.

Magnetic properties of many polynuclear complexes and coordination polymers, containing 3d metal ions bridged by benzenepolycarboxylates, were reported so far,[4] however not so much attention was devoted to the ligands, containing sulfur donor atoms instead of oxygen. Since exchange interactions depend on overlap of magnetic orbitals (the orbitals which bear unpaired electrons),[5] it can be expected that the use of donor atoms able to yield stronger bonds with transition metal ions will favor a more efficient exchange coupling of such metal ions. Bonds involving 3d ions with donor atoms—elements of the 3rd period—are generally characterized by higher covalency compared to those involving the same metal ions with donors from the 2nd period. This can be explained by the lower difference between the energies of atomic orbitals of p- and d-elements.[5] For example, Cu_2, Ni_2, NiCo, and Co_2 dimers with dithiooxamidate bridges revealed significantly higher values of $|J|$ compared to oxalato-bridged analogues.[6] However, at the moment the magnetic properties of Co^{II} and Ni^{II} complexes with bridging sulfur atoms (or multiatomic bridges, involving a sulfur atom) are scarcely studied.[7] This may be due to some synthetic difficulties, including oxidation by air, hydrolytic instability of some sulfur-containing organic molecules, which leads to precipitation of insoluble sulfides, *etc.* In this study we used the dithioamide of 1,3-benzenedicarboxylc acid (hereafter denoted as **m-dtab**), which may be considered as the *S*,*N*-analogue of the well-studied *m*-phthalate. Dithioamide of carboxylic acid was chosen due to its stability to oxidation on air and hydrolytic stability.

---

[a] *L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine. E-mail: shchuk@inphyschem-nas.kiev.ua; Fax: +38 (0)44 525 62 16; Tel: +38 (0)44 525 42 28*
[b] *Equipe Organométalliques et Matériaux Moléculaires, Sciences Chimiques de Rennes, UMR UR1-CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France. E-mail: lahcene.ouahab@univ-rennes1.fr; Fax: +33 (0)2 23 23 68 40; Tel: +33 (0)2 23 23 56 59*

† Dedicated to Prof. Didier Astruc on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Synthesis of ligand, data of electronic spectra of the compounds, details of DFT calculations. CCDC reference numbers 813877–913880. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20173e

Table 1 Crystal data and structure refinement for **m-dtab** and **1–3**

	m-dtab	1	2	3
Empirical formula	$C_8H_8N_2S_2$	$C_8H_8Cl_2CoN_2S_2$	$C_8H_8Br_2CoN_2S_2$	$C_{16}H_{16}Br_2N_4NiS_4$
Formula weight (g mol^{-1})	196.28	326.11	415.03	611.10
Crystal size/mm	0.9 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.2 × 0.1 × 0.1
T/K	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$
a/Å	4.2779(1)	10.513(2)	10.6100(5)	7.912(1)
b/Å	14.0489(6)	15.638(1)	16.1750(6)	10.124(2)
c/Å	14.9941(7)	7.496(1)	7.5080(5)	13.225(2)
β (°)	95.425(3)	104.450(5)	104.83(1)	103.737(1)
Volume/Å^3	897.11(6)	1193.4(3)	1245.58(13)	1029.0(3)
Z	4	4	4	2
Calculated density (g cm^{-3})	1.453	1.815	2.213	1.972
Absorption coefficient (mm^{-1})	0.535	2.201	8.096	5.242
F(000)	408	652	796	604
Theta range for data collection (deg)	1.99 to 30.50	4.05 to 28.70	4.71 to 27.45	3.17 to 27.89
Reflections collected	5287	2988	4764	4591
Reflections unique	2730	1540	1419	2450
R_{int}	0.0428	0.0239	0.0749	0.0527
Goodness-of-fit on F^2	1.020	1.111	1.071	1.003
R_1 $[I > 2\sigma(I)]^a$	0.0601	0.0545	0.0488	0.0538
wR_2 $[I > 2\sigma(I)]^b$	0.1486	0.1352	0.1144	0.1208

^{a} $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$. ^{b} $wR_2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

The aim of this study was to determine if the dithioamide of 1,3-benzenecarboxylic acid (**m-dtab**) can be an efficient mediator of exchange coupling between Co^{II} or Ni^{II} and to study the peculiarities of magnetic properties of coordination polymers, bridged by this thioamide.

In this paper we report three coordination polymers of Co^{II} and Ni^{II}, in which **m-dtab** is coordinated through S-atoms to metal ions: $[Co(m\text{-}dtab)Cl_2\cdot0.65H_2O]_n$ (**1**), $[Co(m\text{-}dtab)Br_2\cdot0.5H_2O]_n$ (**2**) and $[Ni(m\text{-}dtab)_2Br_2\cdot0.25H_2O]_n$ (**3**). X-Ray structures and magnetic properties of the complexes were studied. The efficiency of possible exchange pathways was estimated by DFT calculations, which were consistent with observation of antiferromagnetic ordering at low temperatures for **2** and **3**.

Experimental

Reagents and solvents were commercially available (Aldrich, Merck) and were used without further purification. Hydrogen sulfide was obtained by standard procedure,[8] and the dithioamide of 1,3-benzenecarboxylic acid was prepared by modification of reported procedure[9] (details are provided in supplementary materials‡). Infrared spectra were measured on a Perkin-Elmer Spectrum One spectrometer in the range 400–4000 cm^{-1} in KBr pellets. Electronic spectra were measured on Specord M40 spectrometer in the range 11000–34000 cm^{-1} in $BaSO_4$ matrix pellets. NMR spectra (ligand) were measured on Bruker spectrometer at 500 MHz in DMSO-d_6.

Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer operating in the temperature range 2–300 K with a DC magnetic field up to 5 T. Powdered samples were measured in Teflon tape, intrinsic diamagnetic corrections were calculated using Pascal's constants.[5]

All DFT calculations were performed using ORCA program package.[10] Details of the calculations are provided in supplementary materials.‡

$[Co(m\text{-}dtab)Cl_2\cdot0.65H_2O]_n$ (1)

A solution of 50 mg (0.25 mmol) of **m-dtab** in 5 mL of acetonitrile (some heating may be required for complete dissolving) was added to a solution of 60 mg of $CoCl_2\cdot6H_2O$ (0.25 mmol) in 5 mL of acetonitrile. Dark-green crystals of **1**, which formed in a few days, were filtered off and dried on air. Yield 90%. Anal. Calc. for **1**, $CoCl_2C_8H_{9.3}S_2N_2O_{0.65}$: C, 28.4; H, 2.77; N, 8.3. Found C, 27.9; H, 2.26; N, 8.4%. IR, cm^{-1}: $\nu^{(\text{Thioamide I})}$ 1640 (strong).

$[Co(m\text{-}dtab)Br_2\cdot0.5H_2O]_n$ (2)

This compound was prepared using similar procedure, as for **1**, with $CoBr_2\cdot6H_2O$ (82 mg, 0.25 mmol) instead of $CoCl_2\cdot6H_2O$. Yield 90%. Anal. Calc. for **2**, $CoBr_2C_8H_9S_2N_2O_{0.5}$:C, 22.7; H, 2.14; N, 6.6. Found C, 22.4; H, 1.73; N, 6.4%. IR, cm^{-1}: $\nu^{(\text{Thioamide I})}$ 1634 (strong).

$[Ni(m\text{-}dtab)_2Br_2\cdot0.25H_2O]_n$ (3)

82 mg of $NiBr_2\cdot6H_2O$ (0.25 mmol) were dissolved in 50 mL of boiling acetonitrile, the solution was filtered from undissolved solid and 50 mg (0.25 mmol) of solid **m-dtab** in were dissolved in the hot solution. Reaction mixture was cooled and left undisturbed overnight. Yellowish-orange crystals of **3** were filtered off and dried on air. Yield 50% based on ligand. Anal. calcd for **3**, $NiBr_2C_{16}H_{16.5}S_4N_4O_{0.25}$: C, 31.2; H, 2.7; N, 9.1. Found C, 31.0; H, 2.33; N, 9.0%. IR, cm^{-1}: $\nu^{(\text{Thioamide I})}$ 1623 (strong).

X-Ray structures of ligand **m-dtab** and complexes **1–3** were obtained from single crystals mounted on a Kappa-Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated Mo-Kα radiation source (λ = 0.71069 Å), from the Centre de Diffractométrie (CDIFX), Université de Rennes 1, France. Data were collected at 293 K. Effective absorption correction was performed (SCALEPACK).

Structures of the complexes were solved with direct method using Sir-97[11a] or SIR-2004[11b] software, and refined with full matrix least squares method on F^2 using SHELXL–97 program.[11c] H atoms were placed in idealized positions, except H atoms bounded to N, in compound **1**, that were located on difference Fourier maps. Details of X-ray data collection and refinement are given in Table 1. CCDC 813877–813880 (**1–3** and **m-dtab**, respectively).

Results and discussion

Synthesis

The reaction of $CoCl_2$ or $CoBr_2$ with **m-dtab** in acetonitrile solution led to crystallization of compounds **1** and **2**, respectively. At the same reaction conditions and at the same ratio of reagents, the use of $NiBr_2$ led to precipitation of complex **3**, containing two ligands per metal ion. The attempt to prepare single crystals, suitable for X-ray structure determination, starting from $NiCl_2$ and **m-dtab**, was not successful. The difference in composition of Co^{II} and Ni^{II} complexes (metal-to-ligand ratio) is probably caused by preferred coordination numbers of the metal ions (4 for Co^{II} and 6 for Ni^{II}), as it was shown by X-ray structure determination, *vide infra*. Possible reasons may include different energies of crystal lattice; however there was nothing except the preferred coordination numbers mentioned above, which could obstruct the formation of isostructural Co^{II} or Ni^{II} complexes (as it was found in many cases for Ni^{II} and Co^{II} compounds with identical ligands for coordination numbers from 6,[12] 5[13] and 4[14]).

Complexes **1–3** contain water molecules, which were found by C,H,N analysis, performed on micro-crystalline samples, but which can not be present in the crystal structures, *vide infra*. However, it should be noted that the compounds crystallize as 1D chains built from $[M(m\text{-}dtab)_m(Hal)_2]$ units ($m = 1$ for complexes **1** and **2**, and $m = 2$ for complex **3**), and each $[M(m\text{-}dtab)_m(Hal)_2]$ unit contains a metal ion, and which the coordination sphere is completed by donor atoms of the next monomeric unit. So, at least some water molecules may be captured by the surface of microcrystals or defects in the crystals and complete coordination spheres of metal ions from "terminal" units $M(m\text{-}dtab)_m(Hal)_2$ in 1D chains $[M(m\text{-}dtab)_m(Hal)_2]_n$. Remaining water may be adsorbed on the surface of the microcrystals by physical adsorption forces.

Crystal structures

Dithioamide of 1,3-benzenedicarboxylic acid (ligand **m-dtab**). This compound crystallizes in the $P2_1/c$ space group. The two thioamide groups of **m-dtab** molecule are not crystallographically equivalent (Fig. 1). These molecules are not planar; the angles between the planes of the thioamide groups (mean planes going through C, S, N atoms of the thioamide groups) and the mean plane of aromatic ring are 30.1(2) and 30.3(2)°. On the basis of bonds lengths it may be concluded that C═S bonds are double bonds (1.68 Å on average; selected bond lengths in **m-dtab** along with determination errors are presented in Table 2) and C–N bonds are single (1.32 Å on average), and there is no sign of a possible tautomeric form –C(=NH)SH in the solid state. Thioamide groups of neighboring molecules of **m-dtab** are linked by H-bonds, formed by the H-atom of the NH_2 group of one molecule and the S atom of a neighboring molecule (the distances S(1)–N(1)″ and S(2)–N(2)′ are 3.494(3) and 3.463(3) Å, respectively, Fig. 1). Formation of such H-bonds leads to pseudo-1D zig-zag chains, which are also bonded with similar neighboring chains by H-bonds, also between NH_2 groups and S atoms (the distance S(1)‴–N(2)′ is 3.775(3) Å). Such pseudo-2D layers are located in the (102) plane and parallel planes. The planes of aromatic rings of the adjacent molecules of **m-dtab** in one 2D layer are almost parallel. Finally, the molecules of **m-dtab** from adjacent 2D layers make stacks through π–π interactions of aromatic rings (separation between mean planes of aromatic rings is 3.600(5) **Å**).

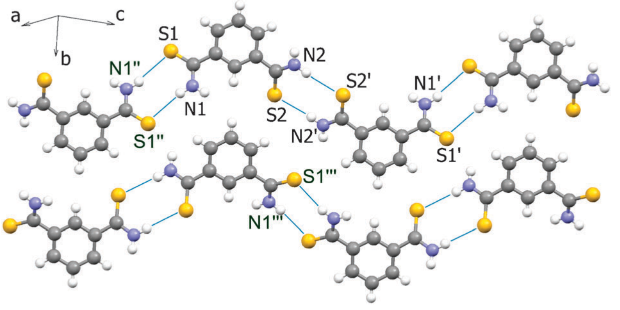

Fig. 1 Crystal structure of **m-dtab**. Two adjacent zig-zag chains are shown. Blue lines indicate H-bonds in zig-zag chain.

Compounds 1 and 2

Compounds **1** and **2** were found to be isostructural and isomorphous, so only the X-ray structure of **1** will be given in Fig. 2. Both complexes crystallize in the $C2/c$ space group. Higher cell dimensions (a, b and c) for **2** compared to **1** are consistent with the higher ionic radius of Br^- compared to Cl^-.

In complex **1** Co^{II} ions are located in pseudo-tetrahedral S_2Cl_2 donor set (S_2Br_2 for compound **2**), where S are sulfur atoms of thioamide groups of two coordinated ligands L (Fig. 2). The positive charge of Co^{II} is counterbalanced by two Cl^- anions (Br^- in **2**). Co^{II} ions are located on C_2 axes, so coordination spheres of these ions are symmetrical. In addition, **m-dtab** ligands in **1** and **2** also have crystallographically imposed twofold symmetry (C3 and C5 atoms being on the C_2 axes). Co–S bonds (2.3146(9) Å in **1** and 2.315(2) Å in **2**, Table 2) are longer than Co–Cl bonds, but shorter than Co–Br ones (Co–Cl 2.257(1) Å in **1** and Co–Br 2.3925(9) Å in **2**). These values are quite typical for tetrahedral Co^{II} complexes with S donors and halides.[15] The angle Cl–Co–Cl (107.88(6)°) is larger than S–Co–S (96.07(5)°) in **1** and similarly, Br–Co–Br (107.95(5)°) is larger than S–Co–S (96.92(8)°) in **2**, and such differences seem to be caused by electrostatic repulsion of negative charges (Cl^- and Br^-) rather than by sterical hindrances.

Two S atoms of each **m-dtab** ligand are coordinated to two Co^{II} ions, so each ligand links two Co^{II} ions, forming infinite 1D chain stretching along [101] direction. (Fig. 2). The shortest distance between adjacent Co^{II} ions within the chain is 11.286(1) Å (11.320(1) Å in **2**), whereas the closest separation

Table 2 Selected structural parameters for **m-dtab**, complexes **1–3** and similar compounds

Compound[a]	Bond length, Å M–S	M–Hal	C=S in thioamide group	C–N in thioamide group	Angle M–S–C in thioamide group, deg	Ref.
m-dtab	—	—	1.678(3), 1.673(3)	1.320(3), 1.319(3)	—	This work
1	2.3146(9)	2.257(1)	1.692(3)	1.312(5)	110.1(1)	This work
2	2.315(2)	2.3925(9)	1.683(6)	1.313(7)	110.1(2)	This work
3	2.462(2), 2.475(2)	2.5820(6)	1.664(6), 1.675(6)	1.328(8), 1.332(8)	120.0(2), 116.5(2)	This work
Ni(DtdtzH$_2$)(ClO$_4$)$_2$	2.384(2),[b] 2.376(2),[b] 2.425(2),[c] 2.411(2)[c]	—	1.698(7), 1.684(7)	1.311(9), 1.310(9)	96.2(2), 96.0(2)[d]	17a
Ni(DtdtzH$_2$)	2.365(1),[b] 2.341(1),[b] 2.412(1),[c] 2.430(1)[c]	—	1.735(4), 1.735(4)	1.344(6), 1.352(6)	93.4(1), 93.9(1)[d]	17a
Ni(TaaH$_2$)$_4$Cl$_2$	2.459(2),[b] 2.458(2)[b]	2.426(1), 2.429(1)	1.682(2), 1.672(2), 1.676(2), 1.685(2)	1.308(1), 1.303(1), 1.313(1)	120.35(5), 116.29(7), 119.07(5), 117.26(7)	17b
[Ni(TaaH$_2$)$_2$-(μ-NCS)$_2$]$_n$	2.446(2)[b]	—	1.701(1)	1.225(1)	113.24(4)	17c
Ni(TaaH$_2$)$_4$Br$_2$	2.224(2),[b] 2.2189(7)[b]	3.600(2)	1.7527(5), 1.6353(3)	1.267(1), 1.3432(9)	113.72(3), 109.67(1)	17d

[a] DtdtzH$_2$ = 4,7-dithiadecane-2,9-dione bis(thiosemicarbazone), TaaH$_2$ = thioacetamide. [b] Thione *S*. [c] Thioether *S*. [d] Involved in chelate cycle.

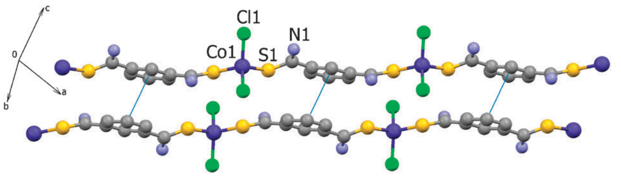

Fig. 2 Crystal structure of **1**. Two adjacent 1D chains are shown. Hydrogen atoms are omitted for clarity. Blue lines show π–π stacking.

between Co^{II} ions from the neighboring chains is 5.4961(8) Å (5.504(1) in **2**).

C=S and C–N bonds of the thioamide group in coordinated **m-dtab** molecules in **1** and **2** are almost the same as in the free ligand, evidencing that the coordination of S atom to metal ions does not have an influence on the character of these bonds (double and single, respectively).

Aromatic rings of **m-dtab** molecules in **1** and **2** seem to be involved in π–π stacking interactions with similar rings of **m-dtab** molecules of neighboring chains in the *c* direction (the distance between mean-square planes of aromatic rings is 3.586(5) Å in **1** and 3.592(5) Å in **2**). SQUEEZE[16] procedure indicated that crystal structures of **1** and **2** contain no voids.

Compound 3

This compound crystallizes in the $P2_1/c$ space group. Ni^{II} ions lie on an inversion center and are located in pseudo-octahedral donor set S$_4$Br$_2$, where S are donor atoms of thioamide groups of four coordinated molecules **m-dtab** (Fig. 3). Positive charges of Ni^{II} ions are compensated by two Br$^-$ ions. Ni–S bond lengths (2.462(2) and 2.475(2) Å, Table 2) are slightly higher (*ca.* 0.05 Å) than previously reported values for Ni–S bonds,[15e,17a–c] while Ni–Br bonds (2.5820(6) Å) are close to Ni–Br bonds in complexes, containing Ni^{II} in octahedral donor sets.[18] Ni–S and Ni–Br bond lengths are quite consistent with the values expected from the sums of ionic radii,[19] despite the fact that the coordination sphere of Ni^{II} contains large Br$^-$ ions and S atoms. Notably, the coordination polyhedron NiS$_4$Br$_2$ in **3** is very different from the one found previously in the complex Ni(TaaH$_2$)$_4$Br$_2$ (with the same coordination environment as in **3**, NiS$_4$(*trans*-Br)$_2$; TaaH$_2$ = thioacetamide).[17d] In the latter compound Ni–S bonds were significantly shorter, than in **3** (2.224(2) and 2.2189(7) Å), while Ni–Br distances were much longer (3.600(2) Å).[17d] However, even in this case high Ni–Br separations are likely to be caused by repulsion of Br$^-$ ions from amino-groups of coordinated thioacetamides rather than by the presence of four "large" S donors.

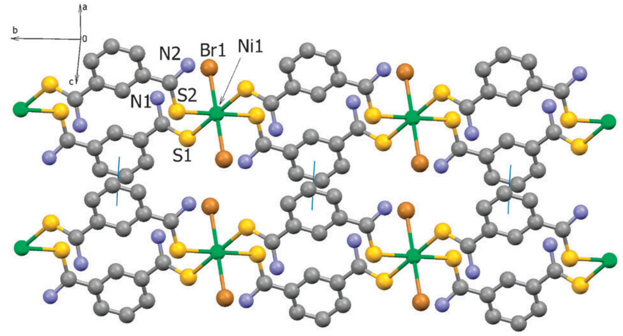

Fig. 3 Crystal structure of **3**. Two adjacent 1D chains are shown. Hydrogen atoms are omitted for clarity. Blue lines show π–π stacking.

Due to centrosymmetry, Br–Ni–Br and S(1)–Ni–S(1) angles are equal to 180°, whereas S(1)–Ni–S(2) angle is 81.27(6)° (inside Ni$_2$(m-dtab)$_2$ metallocycle, Fig. 3) and 98.76(3)° (outside Ni$_2$(m-dtab)$_2$ metallocycle).

It may be concluded from comparison of C=S and C–N bond lengths in **3** and the free ligand that the thioamide groups in **3** possess thione form, similarly to the same ligand in **1** and **2**.

Each **m-dtab** molecule coordinates two Ni^{II} ions through S atoms, acting as a bridging ligand, so each two neighboring Ni^{II} ions are linked by two **m-dtab** molecules. Thus, the compound crystallizes as a 1D chain stretching along the crystallographic *b* axis. The distance between neighboring Ni^{II} ions in the chain is 10.124(2) Å, which is shorter than the intrachain Co–Co separation in **1** and **2** (about 11.3 Å, *vide supra*). The shortest interchain Ni–Ni separation (7.912(1) Å) is about 2 Å longer than the closest interchain Co–Co distance in **1** and **2**.

Similarly to **1** and **2**, the aromatic rings of coordinated **m-dtab** molecules from two adjacent chains are π–π stacked (the distance between mean-square planes of aromatic rings is 3.599(5) Å). As for **1** and **2**, no voids are found in the crystal structure of **3**.

Electronic spectra

The electronic spectrum of thioamide **m-dtab** in solid state reveals a broad maximum centered at 26 300 cm^{-1}, which can be deconvoluted into five Gaussian functions, the lowest of which has a maxima at 21700 and 23500 cm^{-1} (Table S1, supplementary materials‡). The bands with the lowest energy may be assigned to $n \rightarrow \pi^*$ transitions from the n orbital of S to the π^* orbital of the aromatic system, which includes C=S bonds.[20] The explicit views of HOMO and LUMO of **m-dtab**, drawn using Gabedit software[21] (Fig. S1 and S2 in supplementary materials, respectively), are consistent with the assignment of these bands to $n \rightarrow \pi^*$ transitions.

The electronic spectra of the Co^{II} complexes, **1** and **2**, in solid state are typical for complexes of this metal with distorted tetrahedral (C_{2v}) donor sets.[22] Bands in the range 13400–16300 cm^{-1} (Table S1‡) may be assigned to $^4A_2$ (F) → $^4A_2$ (T_1, P) and $^4A_2$ (F) → ^4E (T_1, P) transitions, additionally split by spin–orbit coupling.[22,23] The energies of all such transitions are *ca.* 500–900 cm^{-1} higher in the case of **1** compared to similar transitions in **2** (Table S1), which is consistent with higher crystal field created by Cl^- compared to Br^-. A band at 25 000 cm^{-1} is present in the spectra of both complexes **1** and **2**, and it may be assigned to the intra-ligand transitions (*vide supra*).

Two low-energy bands in the spectrum of Ni^{II} complex **3** at 13100 and 20200 cm^{-1} may be assigned to d–d transitions $^3B_{1g} \rightarrow {}^3B_{2g}$, $^3B_{1g} \rightarrow (^3E_g + {}^3A_{2g})$, respectively (Table S1‡).[22] The band at 25 800 cm^{-1} may originate from both intraligand charge-transfer (*vide supra*) or Ni^{II}-based d–d transitions $^3B_{1g} \rightarrow (^3E_g(P) + {}^3A_{2g}(P))$.

Ni^{II} complexes with similar chromofors NiS_4Hal_2 (where S atoms are donor atoms of macrocyclic or acyclic thioether and $Hal^- = Cl^-, Br^-$) also exhibit three absorption bands in their electronic spectra[24] (Table S1‡). However, all bands in these compounds are observed at lower wavenumbers than in **3** (the difference is about 2000–3000 cm^{-1}). It can be concluded that thioamides create a stronger ligand field than thioethers.

Magnetic properties and evaluation of possible exchange pathways

Magnetic properties of the complexes were characterized by the temperature dependence of the molar magnetic susceptibility, χ_M, from 2 to 300 K in the case of **1** and from 1.8 to 300 K in the case of **2** and **3**. For all complexes $\chi_M T$ decreases with temperature lowering (Fig. 4), evidencing that antiferromagnetic interactions dominate in these compounds.

At 300 K, $\chi_M T$ values for Co^{II} complexes were equal to 2.603 cm^3 K mol^{-1} for **1** and 2.726 cm^3 K mol^{-1} for **2**, which exceeds the expected spin-only value for $S = 3/2$ (1.875 cm^3 K mol^{-1} for $g = 2.0$). At temperature lowering, $\chi_M T$ decreased to 0.534 cm^3 K mol^{-1} for **1** at 2 K and 0.319 cm^3 K mol^{-1} for **2** at 1.8 K. For Ni^{II} complex **3**, $\chi_M T$ value at 300 K was equal to 1.241 cm^3 K mol^{-1}, which also exceeds the expected spin-only value for $S = 1$ (1.000 cm^3 K mol^{-1} for $g = 2.0$). At 1.8 K, $\chi_M T$ for **3** became equal to 0.257 cm^3 K mol^{-1}.

For compound **1**, χ_M monotonously grew with decreasing temperature to 2 K, while for complexes **2** and **3** distinct maxima of χ_M were observed at 2.9 and 2.6 K, respectively, giving evidence for antiferromagnetic ordering (Néel temperature, Fig. 5). It was found that the position of maximum for **3** did not depend on the applied magnetic field in the range between 100 and 800 Oe. Magnetization *vs.* field curves for **2** and **3** at 2 K did not reach saturation (Fig. S3‡).

The existence of antiferromagnetic ordering is possible in the case of magnetic interactions in three dimensions, so it can be concluded that the compounds **2** and **3**, which structurally are 1D polymers, can not be considered as 1D systems at magnetochemical data treatment. Respectively, despite the fact that for all three complexes **1–3** good fits of $\chi_M T$ *vs.* T curves could be obtained using the analytical Fisher's equation[25] based on the model of isotropic ions chains with Heisenberg exchange $H = -J\Sigma S_i S_{i+1} + \Sigma g\beta H S_{zi}$, this approach is not correct and J values, obtained in a such way, have no physical sense. Curie–Weiss fits of $1/\chi_M$ *vs.* T plots gave C = 2.65 cm^3 K mol^{-1} and $\theta = -8.1$ K for **1**, C = 2.78 cm^3 K mol^{-1} and $\theta = -10.1$ K for **2** and C = 1.25 cm^3 K mol^{-1} and $\theta = -3.9$ K for **3** (Curie constants correspond to $g = 2.38$, 2.44 and 2.24 for **1–3**, respectively, Fig. S4‡). θ values for Co^{II} polymers **1** and **2** exceed θ value, reported for similar polymer with *m*-phthalate bridge $[Co(m\text{-}phthalate)(Im)_2]_n$ (−1.86 K).[4a]

The possibility of exchange interactions transfer between metal ions in the compounds from this study through pathways, other than bridging **m-dtab**, was examined by DFT calculations. This approach was shown to be efficient for analysis of magnetic properties.[26] Three models were compared (shown on Fig. S5–S8 on example of compound **1** and described in details in the supplementary materials‡):

(a) exchange interactions between Co^{II} ions through the molecule of **m-dtab** within one 1D chain,

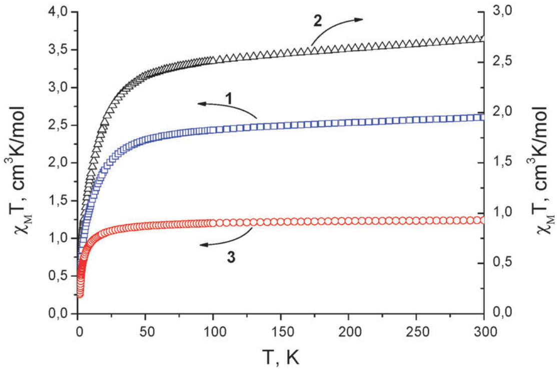

Fig. 4 Experimental $\chi_M T$ *vs.* T plots for **1–3**. Different scales were used for compounds **1** and **2** in order to avoid overlap of the curves.

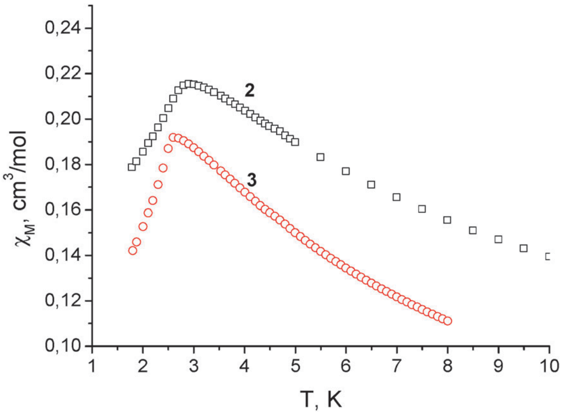

Fig. 5 Experimental χ_M *vs.* T plots for **2** and **3**.

(b) exchange interactions between Co^{II} ions through stacked molecules of **m-dtab** from the neighboring 1D chains, and

(c) exchange interactions between Co^{II} ions through H-bond between N(1) and Cl(1) from the neighboring 1D chains (distance N(1)–Cl(1) is 3.325(3) Å).

BS-DFT calculations of exchange integrals, corresponding to interactions through each of these three pathways, were performed. Though these calculations are not expected to produce the exact values of J parameters, they can be considered as a semi-quantitative estimation of the magnitude and sign of these values.[27] The results (Table 3 and Table S2, S3‡) evidence that the exchange interactions through pathways a) and b) have comparable magnitude, while the exchange through the H-bond (pathway) is negligibly small. It is important, that the coordinates of atoms used for calculations were obtained from X-ray diffraction at room temperature. At lower temperature interchain separations are normally expected to decrease, which should lead to an increase of the efficiency of interchain exchange interactions. Thus, the results of DFT calculations can be considered as the lower estimation of J values. So, the results of calculations confirm that the efficiency of exchange coupling in at least two dimensions is comparable, which is completely consistent with the observation of antiferromagnetic ordering in **2**.

Notably, both exchange pathways a) and b) involve C═S bonds, so these results allow us to make some conclusions regarding transfer of exchange interactions through S atoms. For such analysis, Mayer's bond orders[31] for some bonds in **1** were calculated (Table S5‡). Compound [Co(*m*-phthalate)(Im)$_2$]$_n$ (Im = imidazole) reported by Song *et al.*[4a] was analyzed for comparison, because it seems to be the most similar to polymers with dithioamide among the variety of reported polymeric *m*-phthalates. The calculations showed that the Co–S bond order in **1** (0.6505) was higher than the Co–O bond order in [Co(*m*-phthalate)(Im)$_2$]$_n$ (0.516 in average), confirming that in the first approximation the covalency of the Co–S bond is higher than in the case of Co–O bond. Also, as it was already concluded from the analysis of bond lengths (see X-ray structures description), the C═S bond in the thioamide group (neutral) in **1** has more double character than C–O bond in carboxylate (deprotonated carboxylic) group in [Co(*m*-phthalate)(Im)$_2$]$_n$ (Mayer's bond orders 1.538 and in average 1.374, respectively, Table S5). Because of the lack of numerical values of J, we can conclude that the efficiency of exchange interactions through the S donor is at least comparable with exchange interactions through the O donor. These results are consistent with previous findings from the studies of dimers with thiooxamides.[6]

Concluding remarks

Nickel(II) and cobalt(II) coordination polymers with **m-dtab** were synthesized and characterized. To the best of our knowledge, these compounds are the first representatives of complexes with a bridging dithioamide of an aromatic dicarboxylic acid. Despite of the fact that the compounds **1–3** crystalize as 1D chains, their magnetic properties provide evidence for the existence of comparable exchange interactions in several directions, which result in antiferromagnetic ordering at 2.9 and 2.6 K for **2** and **3**, respectively. This is consistent with the results of DFT calculations, which show that the exchange interactions through bridging **m-dtab** in a 1D chain or through π–π stacking of aromatic rings between the chains have comparable magnitude. Since all possible pathways of exchange coupling involve S atoms, we can conclude that it can efficiently mediate exchange interactions.

Table 3 Results of DFT calculations of J values for model compounds, representing binuclear fragments of **1** and **2** (using TPSS functional, details are presented in supplementary materials‡)

Compound	Basis	Pathway[a]	E_{HS}–E_{BS}, cm^{-1}	J_1,[b] cm^{-1}	J_2,[b] cm^{-1}	J_3,[b] cm^{-1}
1	def2-SVP	Co-(m-dtab)-Co	1.511	−0.17	−0.13	−0.17
		π-stacking	1.999	−0.22	−0.17	−0.22
		H-bond	0.285	−0.03	−0.02	−0.03
	def2-TZVP	Co-(m-dtab)-Co	2.028	−0.23	−0.17	−0.23
		π-stacking	2.634	−0.29	−0.22	−0.29
		H-bond	0.194	−0.02	−0.02	−0.02
2	def2-SVP	Co-(m-dtab)-Co	1.414	−0.16	−0.12	−0.16
		π-stacking	1.977	−0.22	−0.16	−0.22
		H-bond	0.060	−0.01	0.00	−0.01
	def2-TZVP	Co-(m-dtab)-Co	1.904	−0.21	−0.16	−0.21
		π-stacking	2.617	−0.29	−0.22	−0.29
		H-bond	−0.177	0.02	0.01	0.02

[a] exchange pathways are described in the text and shown on Fig. S5. [b] J_1, J_2 and J_3 refer to different schemes of J calculation using HS-BS gap: J_1–after Ginsberg, Noodleman and Davidson ($J_1 = -(E_{HS}-E_{BS})/S^2_{max})$),[28] J_2 – after Bencini and Gatteschi ($J_2 = -(E_{HS} - E_{BS})/(S_{max}(S_{max} + 1))$))[29] and J_3—after Yamaguchi, Takahara, Fueno and Soda ($J_3 = -(E_{HS}-E_{BS})/(\langle S^2_{HS}\rangle - \langle S^2_{BS}\rangle)$))).[30]

Acknowledgements

A.S.L. thanks to Rostyslav Dolog for help in comprehension of *ab initio* and DFT calculation methods and to ORCA team and community (and especially to Prof. Frank Neese) for helpful answers about ORCA usage. S.V.K. thanks CNRS for invited researcher position in UMR 6226 Rennes. Work partially supported by CNRS, University of Rennes 1, Région Bretagne and by joint grant of the National Academy of sciences of Ukraine and CNRS.

References

1 Selected examples: (*a*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*b*) D. Maspoch, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; (*c*) X.-Y. Wang, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2008, 281; (*d*) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.

2 (*a*) R. Robson, *Dalton Trans.*, 2008, 5113; (*b*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (*c*) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239; (*d*) M. J. Rosseinsky, *Microporous Mesoporous Mater.*, 2004, **73**, 15; (*e*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*f*) S. V. Kolotilov, O. Cador, K. S. Gavrilenko, S. Golhen, L. Ouahab and V. V. Pavlishchuk, *Eur. J. Inorg. Chem.*, 2010, 1255; (*g*) E. Pardo, J. Faus, M. Julve, F. Lloret, M. C. Muñoz, J. Cano, X. Ottenwaelder, Y. Journaux, R. Carrasco, G. Blay, I. Fernández and R. Ruiz-García, *J. Am. Chem. Soc.*, 2003, **125**, 10770; (*h*) T. R. Felthouse, E. N. Duesler and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1978, **100**, 618; (*i*) T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2636; (*j*) G. Dong, Q. Chun-qi, D. Chun-ying, P. Ke-liang and M. Qing-Jin, *Inorg. Chem.*, 2003, **42**, 2024.

3 (*a*) H. W. Park, S. M. Sung, K. S. Min, H. Bang and M. P. Suh, *Eur. J. Inorg. Chem.*, 2001, 2857; (*b*) M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Moratal, A. Monge and E. Gutierrez-Puebla, *Inorg. Chem.*, 1987, **26**, 3520; (*c*) M. S. Haddad, D. N. Hendrickson, J. P. Cannady, R. S. Drago and D. S. Bieksza, *J. Am. Chem. Soc.*, 1979, **101**, 898; (*d*) S. V. Kolotilov, O. Cador, S. Golhen, O. Shvets, V. G. Ilyin, V. V. Pavlishchuk and L. Ouahab, *Inorg. Chim. Acta*, 2007, **360**, 1883; (*e*) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Coôté, J. Kim and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 7110; (*f*) V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, M. J. Prushan, R. J. Butcher and L. K. Thompson, *Chem. Commun.*, 2002, 468.

4 Selected examples: (*a*) J.-F. Song, Y. Chen, Z.-G. Li, R.-S. Zhou, X.-Y. Xu and J.-Q. Xu, *J. Mol. Struct.*, 2007, **842**, 125; (*b*) C.-K. Xia, C.-Z. Lu, D.-Q. Yuan, Q.-Z. Zhang, X.-Y. Wu, S.-C. Xiang, J.-J. Zhang and D.-M. Wu, *CrystEngComm*, 2006, **8**, 281; (*c*) Y.-Z. Zheng, Y.-B. Zhang, M.-L. Tong, W. Xue and X.-M. Chen, *Dalton Trans.*, 2009, 1396; (*d*) F. Luo, Y. Che and J. Zheng, *Cryst. Growth Des.*, 2009, **9**, 1066; (*e*) J. Klingele, M. H. Klingele, O. Baars, V. Lozan, A. Buchholz, G. Leibeling, W. Plass, F. Meyer and B. Kersting, *Eur. J. Inorg. Chem.*, 2007, 5277; (*f*) P.-K. Chen, Y.-X. Che and J.-M. Zheng, *Inorg. Chem. Commun.*, 2007, **10**, 187; (*g*) X.-N. Cheng, W.-X. Zhang, Y.-Y. Lin, Y.-Z. Zheng and X.-M. Chen, *Adv. Mater.*, 2007, **19**, 1494.

5 O. Kahn, *Molecular Magnetism*, VCH, 1993.

6 (*a*) J. Cano, E. Ruiz, P. Alemany, F. Lloret and S. Alvarez, *J. Chem. Soc., Dalton Trans.*, 1999, 1669; (*b*) F. Březina, Z. Šindelář, L. Kvítek and R. Pastorek, *Transition Met. Chem.*, 1999, **24**, 88; (*c*) E. A. Mikhalyova, A. W. Addison, S. V. Kolotilov, V. V. Pavlishchuk, O. Cador, M. Zeller, W. G. Dougherty Jr., L. Ouahab, A. D. Hunter and S. Trofimenko, *Abstracts of Papers, 237th American Chemical Society National Meeting*, Salt Lake City, UT, United States, March 22-26, 2009, INOR-169.

7 (*a*) G. A. Melson, N. P. Crawford and B. J. Geddes, *Inorg. Chem.*, 1970, **9**, 1123; (*b*) F. Březina, Z. Šindelář, L. Kvítek and R. Pastorek, *Transition Met. Chem.*, 1999, **24**, 88; (*c*) A. Castiñeiras, M. C. F. Vidal, J. Romero, R. Sáez, A. Matilla, J. Niclós and J. M. Tercero, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1553; (*d*) S. G. Carling, J. M. Bradley, D. Visser and P. Day, *Polyhedron*, 2003, **22**, 2317; (*e*) A. Gleizes and M. Verdaguer, *J. Am. Chem. Soc.*, 1981, **103**, 7373; (*f*) M. Verdaguer, A. Gleizes, J. P. Renard and J. Seiden, *Phys. Rev. B*, 1984, **29**, 5144.

8 G. Brauer, *"Handbook of Inorganic Synthesis"*, Mir, Moscow, 1985, vol. 2, p. 395.

9 V. A. Mamedov, Y. A. Levin, E. K. Trutneva, A. T. Gubaidullin, I. Kh. Rizvanov, E. Ya. Levina, I. A. Litvinov and Y. Ya. Efremov, *Arrkivoc*, 2004, **XII**, 47.

10 F. Neese, *ORCA–an* ab initio, *Density Functional and Semiempirical program package, Version 2.8.0*, University of Bonn, 2010.

11 (*a*) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115; (*b*) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381; (*c*) G. M. Sheldrick, *SHELX-97: University of Göttingen*, Göttingen, Germany, 1997.

12 (*a*) M. H. Klingele and S. Brooker, *Coord. Chem. Rev.*, 2003, **241**, 119; (*b*) H.-F. Zhu, W.-Y. Sun, T.-A. Okamura and N. Ueyama, *Inorg. Chem. Commun.*, 2003, **6**, 168; (*c*) J.-M. Rueff, S. Pillet, N. Claiser, G. Bonaventure, M. Souhassou and P. Rabu, *Eur. J. Inorg. Chem.*, 2002, 895; (*d*) D. L. Reger, C. A. Little, M. D. Smith and G. J. Long, *Inorg. Chem.*, 2002, **41**, 4453; (*e*) F.-T. Xie, L.-M. Duan, J.-Q. Xu, L. Ye, Y.-B. Liu, X.-X. Hu and J.-F. Song, *Eur. J. Inorg. Chem.*, 2004, 4375.

13 A. V. Yakovenko, S. V. Kolotilov, A. W. Addison, S. Trofimenko, G. P. A. Yap, V. Lopushanskaya and V. V. Pavlishchuk, *Inorg. Chem. Commun.*, 2005, **8**, 932.

14 K. Uehara, S. Hikichi and M. Akita, *J. Chem. Soc., Dalton Trans.*, 2002, 3529.

15 (*a*) A. H. Mahmoudkhani and V. Langer, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **58**, m592; (*b*) C. A. Bremner and W. T. A. Harrison, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, m425; (*c*) B. F. Ali, R. H. Al-Far and S. F. Haddad, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, m485; (*d*) H. Zhang, L. Fang and R. Yuan, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m609; (*e*) W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266; (*f*) S. C. Shoner, A. M. Nienstedt, J. J. Ellison, I. Y. Kung, D. Barnhart and J. A. Kovacs, *Inorg. Chem.*, 1998, **37**, 5721.

16 (*a*) A. L. Spek, *Acta Crystallogr., Sect A*, 1990, **46**, C34; (*b*) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

17 (*a*) V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 2000, 335; (*b*) R. L. Girling, J. E. O'Connor and E. L. Amma, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 2640; (*c*) L. Capacchi, G. F. Gasparri, M. Nardelli and G. Pelizzi, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 1199; (*d*) W. A. Spofford III, P. Boldrini and E. L. Amma, *Inorg. Chim. Acta*, 1971, **5**, 70.

18 (*a*) J. C. Barnes and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.*, 1976, 1786; (*b*) J. W. Steed, B. J. McCool and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 1998, 3417; (*c*) M. E. Masaki, B. J. Prince and M. M. Turnbull, *J. Coord. Chem.*, 2002, **55**, 1337.

19 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751.

20 L. A. Kazitsina and N. B. Kupletskaya, *The Use of UV-, IR-, NMR and Mass-Spectroscopy in Organic Chemistry*, 2nd edn, Publishing House of Moscow University, 1979.

21 A. R Allouche, *J. Comput. Chem.*, 2011, **32**, 174.

22 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1984.

23 J. V. Quagliano, A. K. Banerjee, V. L. Goedken and L. M. Vallarino, *J. Am. Chem. Soc.*, 1970, **92**, 482.

24 (*a*) W. Rosen and D. H. Busch, *J. Chem. Soc. D*, 1969, 148; (*b*) W. Levason, Ch. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1975, 1566.

25 (*a*) M. E. Fisher, *Am. J. Phys.*, 1964, **32**, 343; (*b*) K.-Y. Choi and K.-J. Kim, *Polyhedron*, 2008, **27**, 1311.

26 (*a*) J. J. Novoa, M. Deumal and J. Jornet-Somoza, *Chem. Soc. Rev.*, 2011, **40**, 3182; (*b*) R. Bast, U. Ekstroöm, B. Gao, T. Helgaker,

K. Ruud and A. J. Thorvaldsen, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2627; (*c*) M. A. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin and E. Colacio, *Inorg. Chem.*, 2010, **49**, 10156; (*d*) Y.-Q. Zhang, C.-L. Luo and Z. Yu, *New J. Chem.*, 2005, **29**, 1285.

27 I. Ciofini and C. A. Daul, *Coord. Chem. Rev.*, 2003, **238–239**, 187.

28 (*a*) A. P. Ginsberg, *J. Am. Chem. Soc.*, 1980, **102**, 111; (*b*) L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737; (*c*) L. Noodleman and E. R. Davidson, *Chem. Phys.*, 1985, **109**, 131.

29 A. Bencini and D. Gatteschi, *J. Am. Chem. Soc.*, 1980, **108**, 5763.

30 K. Yamaguchi, Y. Takahara and T. Fueno, in *Applied Quantum Chemistry*, ed. V. H. Smith, Reidel, Dordrecht, 1986, p. 155; T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett.*, 2000, **319**, 223.

31 A. J. Bridgeman, G. Cavigliasso, L. R. Ireland and J. Rothery, *J. Chem. Soc., Dalton Trans.*, 2001, 2095.