Charge Transfer Salts of BO with Paramagnetic Isothiocyanato Complex Anions: (BO)[M(isoq)$_2$(NCS)$_4$]; M=Cr^{III} or Fe^{III}, isoq=isoquinoline and BO=Bis(ethylenedioxo)tetrathiafulvalene

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The preparation, X-ray structures and magnetic properties of two isostructural new charge transfer salts: (BO)[M(isoq)$_2$(NCS)$_4$]; M = Cr^{III} (1), Fe^{III} (2) and isoq = isoquinoline are reported. Their structure consists of alternate organic and inorganic layers, each layer being formed by mixed columns of BO radical cations and paramagnetic metal complex anions. There are short intermolecular contacts between donor and anion (S2$_{anion}$···S4$_{BO}$ < 3.5 Å) and between adjacent BO molecules (O···O1 < 3.2 Å). The two compounds are insulators. ESR measurements show single signal without separating the donor and anion spins. The magnetic measurements obey the Curie–Weiss law and revealed dominant antiferromagnetic interactions between anion spin and donor spin, but long-range magnetic ordering did not occur down to 2 K. This is directly related to structural reasons which were deduced from a comparison of the title compounds with other 1:1 salts containing same anion complexes and different donors. © 2002 Elsevier Science (USA)

Key Words: BEDO-TTF or BO; Isothiocyanato complex; chromium; iron; crystal structure; magnetism; ESR.

INTRODUCTION

Radical cation salts and charge transfer (CT) complexes based on tetrathiafulvalene (TTF) and its derivatives provide a wide class of organic materials with particular properties ranging from insulating to superconducting (1). In the last few years an increased interest was devoted to multifunctional materials aiming to obtain synergy between two physical properties in the same compound. For the particular class of materials combining electrical conductivity and magnetic interactions, it is hoped to achieve magnetic coupling between the localized spin of the inorganic part (*d*-electrons) through the mobile electrons of the organic part (π-delectrons) via the so-called π–*d* interactions (2–11). Most of the known materials show a coexistence of two independent conducting and magnetic lattices and the magnetic interactions, when found, are not mediated by the conducting electrons. For example, (BEDT–TTF)$_4$[(H$_3$O)Fe(C$_2$O$_4$)$_3$]C$_6$H$_5$CN (3), (BEDT–TTF = bis(ethylenedithio)tetrathiafulvalene) and (BETS)$_2$(FeCl$_4$)$_{0.5}$(GaCl$_4$)$_{0.5}$ (4), (BETS = bis(ethylenedithio)tetraselenafulvalene) are superconducting paramagnets with T_c = 8.5 and 4.6 K, respectively. More recently, coexistence of metallic state and long-range ferromagnetic ordering has been found in (BEDT–TTF)$_3$[MnCr(C$_2$O$_4$)$_3$] (9a) and (BO)$_3$[FeCr(C$_2$O$_4$)$_3$] (9b) (bis(ethylenedioxo)tetrathiafulvalene), but the magnetic coupling is not mediated by the conducting electrons. Only in few cases interactions between the π and *d* electrons were claimed as for instance in the series of BETS salts (4) and also in (DMET)$_2$FeBr$_4$ (DMET = 4,5-ethylenedithio-4′,5′-dimethyl-1,3-dithia-1′,3′-diselenafulvalene) (6c,6d). In order to establish magnetic and/or structural interactions between the organic and inorganic sublattices, several ways are under investigation. Using thiocyanato-complexes [M^{III}(NCS)$_4$(L)$_n$]$^-$ where L = 1,10-phenanthroline (phen) n = 1 or isoquinoline (isoq) n = 2, which can enable both S···S and π···π interactions between the conducting and magnetic systems, Day's group obtained bulk ferrimagnetism in TTF-based salts with T_c's ranging from 4.2 to 8.9 K (10). With the same anions combined to tetrathiapentalene-based donors that are non-TTF donors we obtained recently bulk weak ferromagnetism in (BDH–TTP)[M(NCS)$_4$(isoq)$_2$], M = Cr^{III} and Fe^{III} (BDH–TTP stands for 2,5-bis-(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene) (11).

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Continuing our efforts in this line, we prepared new CT salts with the above-mentioned transition metal complex anions and BO, a BEDT–TTF analogue with four peripheral oxygen atoms. It is known that this donor molecule gives organic metals almost exclusively due to the self-assembly property in the CT salts (12, 13). We report here the preparation, X-ray crystal structures and magnetic properties of two new salts based on this donor and paramagnetic thiocyanato-complex anions, namely (BO)[M(isoq)$_2$(NCS)$_4$]; $M = Cr^{III}$ $S = \frac{3}{2}$ [compound (**1**)], Fe^{III} $S = \frac{5}{2}$ [compound (**2**)]. A comparison of the crystal structure of these compounds with those of two other 1:1 salts, namely BEDT-TTF[Cr^{III}(isoq)(NCS)$_4$](10d) and BDH–TTP[M^{III}(isoq)(NCS)$_4$] (11) is given in order to explain the difference in their magnetic properties.

EXPERIMENTAL

Synthesis

All experiments were conducted under nitrogen or argon. The solvents were distilled before use and the starting reagents were used as received. (isoqH)[Cr(isoq)$_2$(NCS)$_4$] · 3H$_2$O, (Bu$_4$N)[Fe(isoq)$_2$(NCS)$_4$] · 3H$_2$O and BO, were prepared following published methods.(10,13). The stoichiometries of target materials were determined by X-ray crystal structure analysis. (BO)[M(isoq)$_2$(NCS)$_4$]; $M = Cr^{III}$ (**1**), Fe^{III} (**2**): the two compounds were prepared in the same conditions. Black crystals were obtained by galvanostatic oxidation after 1 week using BO (8 mg, 2.1 × 10^{-2} mmol), platinum wire electrodes ($\varnothing = 1$ mm) and a constant current intensity of ca. 1.0 μA. Solutions of (isoqH)[Cr (isoq)$_2$(NCS)$_4$] · 3H$_2$O (100 mg, 0.137 mmol) for **1** and (Bu$_4$N)[Fe(isoq)$_2$(NCS)$_4$] · 3H$_2$O (100 mg, 0.126 mmol) for **2**, in CH$_2$Cl$_2$ (20 mL) were used as electrolyte.

Crystallographic Data Collection and Structure Determination

Single crystals of title compounds (**1–2**) were mounted on an Enraf-Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated Mo$K\alpha$ radiation source ($\lambda = 0.71073$ Å). Data collection was performed at room temperature. No absorption correction were carried out and structures were solved with SHELXS-97 (14) and refined with SHELXL–97 (14) programs by full matrix least-squares method, on F^2.

Crystallographic data are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publications no CCDC No. 176075 and No. 181704. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2

TABLE 1
Crystal Data and Structure Refinement for (1) and (2)

	(1)	(2)
Empirical formula	C$_{32}$H$_{22}$CrN$_6$O$_4$S$_8$	C$_{32}$H$_{22}$FeN$_6$O$_4$S$_8$
Formula weight	863.04	866.89
Radiation, λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	7.937(3)	7.898(3)
b(Å)	9.702(4)	9.719(4)
c(Å)	12.243(6)	12.258(6)
α (deg)	92.33(2)	92.33(2)
β (deg)	98.15(2)	98.15(2)
γ (deg)	104.56 (2)	104.56(2)
V (Å^3),	900.5 (7)	898.7(2)
D_{calc} (g cm^{-3})	1.591	1.602
Z	1	1
μ (mm^{-1})	0.829	0.932
Reflections $I > 2\sigma(I)$	4051	3235
Final R_1, wR_2	0.0502, 0.1106	0.0572, 0.1136

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Magnetic Measurements

ESR spectra were recorded with a JEOL JES TE-200 X-band Spectrometer equipped with Oxford ESR910 cryostat. Magnetic susceptibility measurements were performed on powdered microcrystalline sample enclosed in polyethylene film with a Quantum Design MPMS-XL SQUID magnetometer.

RESULTS AND DISCUSSION

Crystal Structures

Selected bond distances and bond angles are given in Table 2. ORTEP drawings of the molecular structure for (**1**) with the atomic numbering scheme is shown in Fig. 1.

Since the two compounds are isostructural, we describe here the structure of compound **1** and we give the data for compound **2** in brackets. The assymetric unit contains one anion and one BO molecule both in special positions, (0, 0, 0) and ($\frac{1}{2}$, 0, $\frac{1}{2}$), respectively. The $M-$N (of NCS) distances (mean value 1.988(3) [2.031(5)] Å) are slightly shorter than those to isoquinoline ($M-$N3 = 2.081(3) [2.145(4)] Å). From the 1:1 stoichiometry, the charge on the BO molecule is assumed equal to ca. +1. The crystal structure (Fig. 1b) can be described following two ways: (i) It can be viewed as alternate organic and inorganic layers along the b direction, the organic layer (**I** in Fig. 1b) containing both BO molecules and isoquinoline ligands and the inorganic layer containing M(NCS)$_4$ units. (ii) It can be viewed also as successive mixed organic–inorganic layers (**II** in Fig. 1b) in the [$\bar{1}$10] direction. Short contacts,

	(1)	(2)
M–N(2)	1.987(3)	2.036(4)
M–N(1)	1.988(3)	2.027(5)
M–N(3)	2.081(3)	2.145(4)
S(4)–C(12)	1.718(4)	1.728(6)
S(4)–C(14)	1.731(4)	1.713(6)
S(3)–C(13)	1.725(4)	1.722(7)
S(3)–C(12)	1.728(4)	1.731(5)
O(2)–C(14)	1.358(5)	1.328(7)
O(2)–C(16)	1.450(6)	1.442(7)
O(1)–C(13)	1.358(5)	1.342(6)
O(1)–C(15)	1.443(5)	1.439(8)
C(2)–S(2)	1.611(3)	1.611(6)
C(1)–S(1)	1.616(4)	1.606(6)
C(12)–C(12)^i	1.380(8)	1.351(11)
N(2)–M–N(1)	88.12(13)	89.63(2)
N(2)–M–N(3)	88.86(11)	88.72(2)
N(1)–M–N(3)	89.91(12)	90.40(18)
C(12)–S(4)–C(14)	94.36(19)	94.5(3)
C(13)–S(3)–C(12)	94.23(19)	93.7(3)
C(14)–O(2)–C(16)	109.7(3)	109.6(5)
C(13)–O(1)–C(15)	111.4(3)	111.0(5)
C(1)–N(1)–Cr	165.1(3)	165.0(5)
C(2)–N(2)–Cr	159.5(3)	154.7(5)

Note. i: $-x, -y+1, -z+1$.

$S2_{anion}\cdots S4_{BO} = 3.489(2)$ [3.497(3)] Å (the sum of van der Waals radii (vdW) = 3.60 Å) are present between anion and donor (Fig. 1b). The shortest contacts between adjacent BO units belonging to adjacent mixed layers in the [-110] direction (Fig. 1b) are in the vdW range ($S4_{BO}\cdots O2_{BO} = 3.325(3)$ [3.356(5)] Å (sum of vdW = 3.32 Å)). The side view of the organic layer (**I**) is depicted in Fig. 2a. It consists of π stacking mixed columns of BO radical cations and isoquinoline ligands parallel to the c direction. The interplanar separations between adjacent isoquinoline–isoquinoline and BO–isoquinoline units are $d1 = 3.549(4)$ [3.532(6)]Å and $d2 = 3.642(5)$ [3.637(6)]Å, respectively. A side-by-side arrangement of the BO units is also observed in the a direction. The projection of the mixed organic and inorganic layer (**II**) in the bc plane is shown in Fig. 2b. It reveals the existence of separated columns of radical cations and anion complexes parallel to the b direction and each layer consists of successive columns along the c direction. In the [011] direction (Fig. 2b), a mixed chain of anion and radical cation is found, the shortest $S_{anion}\cdots S_{BO}$ contact is $S2\cdots S4 = 3.713(3)$ [3.717(3)] Å (not shown in the figure) which is longer than sum of vdW radii. The most significant contact $O1_{BO}\cdots O1_{BO} = 3.187(2)$ [3.194(8)]Å takes place in the b direction (Fig. 2b) between adjacent molecules which have head-to-tail arrangement. We should point out therefore that in our compound, the BO molecules are isolated, i.e,

they do not form π stacking. This is different from the previously known 1:1 salt namely, $(BO)I_3$ (15), where the $+1$ ionized organic molecules form dimers. But a similar situation was encountered in $(BO)(I_3)_2$ salt containing doubly charged BO^{2+} units (15).

Electrical, Magnetic and ESR Properties

The four-probe electrical conductivity was measured on compressed pellet at room temperature. The resistance values are so high (over $1.5\,\text{G}\Omega\,\text{cm}$) and therefore the compounds are good insulators which is expected for 1:1 stoichiometry with complete ionicity for donor molecules. The temperature dependences of the magnetic suscepti-bility for the title compounds were measured in the temperature range 2–300 K, with an applied field of 100 Oe. The plots of $\chi_M T$ versus T are shown in Fig. 3 for (**1**) and (**2**), respectively (χ_M is the molar magnetic susceptibility corrected for the core diamagnetism (for diamagnetic contributions see Ref. (16) and T is the temperature).

For compound (**1**), the susceptibility obeys a Curie–Weiss law above 10 K with the Curie constant $C = 2.59\,\text{emu K mol}^{-1}$ ($\Theta = -7.18$ K) which is somehow higher than the spin-only value of $2.25\,\text{emu K mol}^{-1}$ for non-interacting anion ($S = \frac{3}{2}$) and donor ($S = \frac{1}{2}$) spins. Below 100 K, the $\chi_M T$ value decreases to reach a value of ca. $1.05\,\text{emu K mol}^{-1}$ at 2 K. This value might correspond to what is expected when the anion and donor spins are antiferromegnetically coupled. For compound (**2**), the susceptibility also obeys a Curie–Weiss law above 50 K with the Curie constant $C = 4.88\,\text{emu K mol}^{-1}$ ($\Theta = -1.69$ K) which is very close to the value of $4.75\,\text{emu K mol}^{-1}$ expected for two non-interacting anion ($S = \frac{5}{2}$) and donor ($S = \frac{1}{2}$) spins. Below 100 K, $\chi_M T$ decreases as the temperature decreases down to 4.5 K, showing the antiferromagnetic coupling between the anion ($S = \frac{5}{2}$) and donor ($S = \frac{1}{2}$) spins. But before reaching to the value of 3.00, which is expected for the antiparallel alignment of the anion and donor spins, $\chi_M T$ shows a steep increase from 4.5 down to 2 K. This might originate from paramagnetic impurities or from the onset of a long-range ferrimagnetic ordering occurring below 2 K. To check this last point, we performed the field dependence magnetizations at $T = 2$ K for (**1**) and (**2**), respectively (see supplementary material). As the field increases, the magnetizations tend to saturate and reach at 5 T the values of $3.50\,\mu_B$, and $4.72\,\mu_B$, respectively, for (**1**) and (**2**). These values are somehow smaller than those expected for the full orientation of the magnetic spins on BO and the transition metal ions ($4\,\mu_B$, for **1** and $6\,\mu_B$ for **2**). The reason why we could not observe the theoretical values may be (i) the applied magnetic field was not enough, (ii) the sample contained some non-magnetic impurities. Additionally, we did not detect any hysteretic behaviors. This exclude the
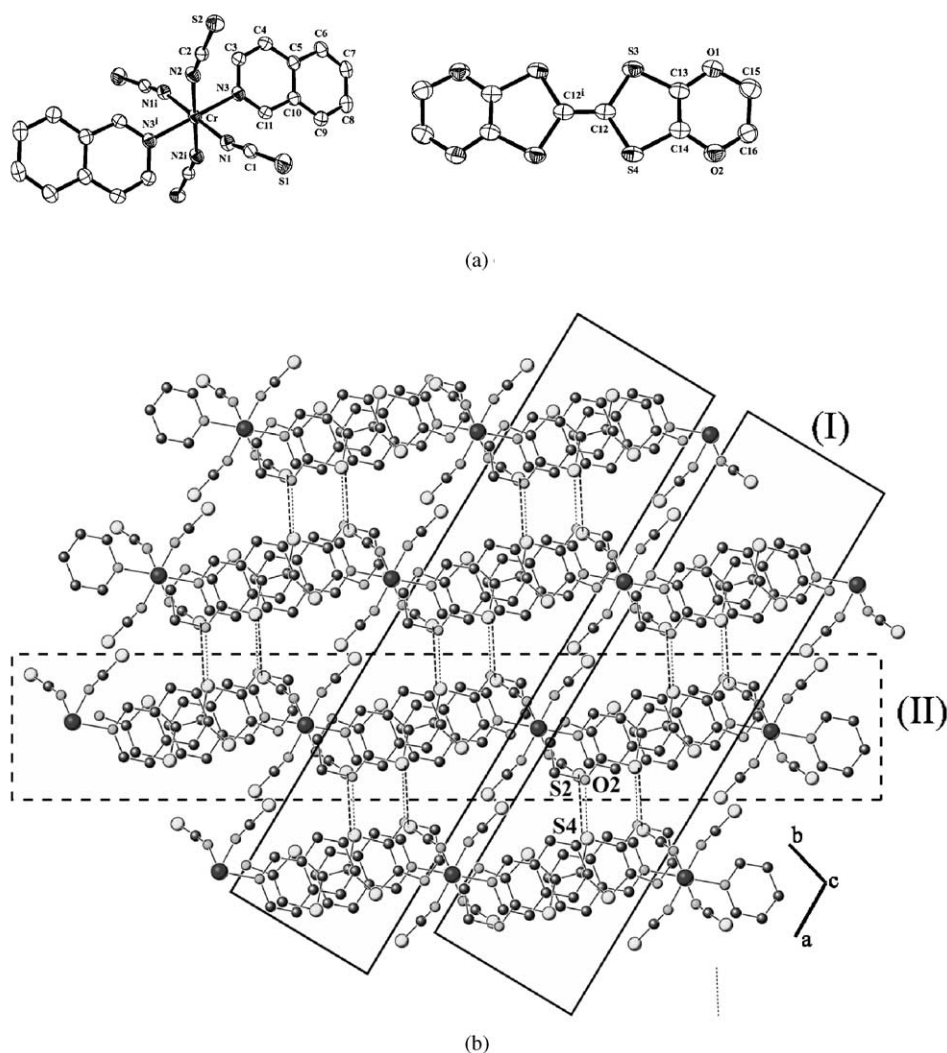
(a)

(b)

FIG. 1. (a) ORTEP diagram with 50% probability level and atom numbering scheme, (b) Projection of the crystal structure onto the *ab* plane, showing the π overlap between the isoquinoline ligands and the BO molecules. Square with full lines (**I**) indicate the organic layers, square with dashed lines (**II**) indicate the mixed anion-donor layers. The interlayer contacts are also shown S2$\cdots$S4 = 3.489(2) [3.497(2)] Å (dashed lines) and O2$\cdots$S4 = 3.325(3) [3.356(5)] Å (dotted lines).

occurrence of any long-range magnetic ordering in the low-temperature domain. For both compounds (**1**) and (**2**), the ESR spectra on microcrystalline samples give single Lorentzian signals without separating the contributions of the donor and anion spins. This suggests the presence of the exchange interaction between these two spin species. The ESR signal data at room temperature are $g = 1.9804$ and $\Delta H = 128.6$ mT for (**1**) and $g = 2.0483$ and $\Delta H = 132.2$ mT for (**2**). These g-values are close to those found for Cr^{3+} ion (1.999) in $[K_3Cr(CN)_6]$ (17) and for high-spin Fe^{3+} (2.0256) in $(Bu_4N)[Fe(isoq)_2(NCS)_4] \cdot 3H_2O$. The line shape of the ESR signal is mainly governed by the anion spins, though the cation must have contributions judging from the total spin susceptibility.

The question we are faced with is why these two BO-based compounds do not exhibit long range ferri- or ferromagnetic interactions as other CT salts with same anions, namely BEDT–TTF[Cr^{III}(isoq)(NCS)$_4$] (10) and BDH–TTP[Cr^{III}(isoq)(NCS)$_4$] (11). The answer to this question can be found in the structure–property relationships, since the intermolecular overlap integral can be strongly modulated by the small change of the crystal structure (18). Both of these compounds have layered structures and the layer consists of mixed chains of donors and anions reminiscent to that depicted in Fig. 2b. These salts have the same 1:1 stoichiometry, but a careful examination of their crystal structures revealed slight differences: (i) in the mixed anion-donor chains several
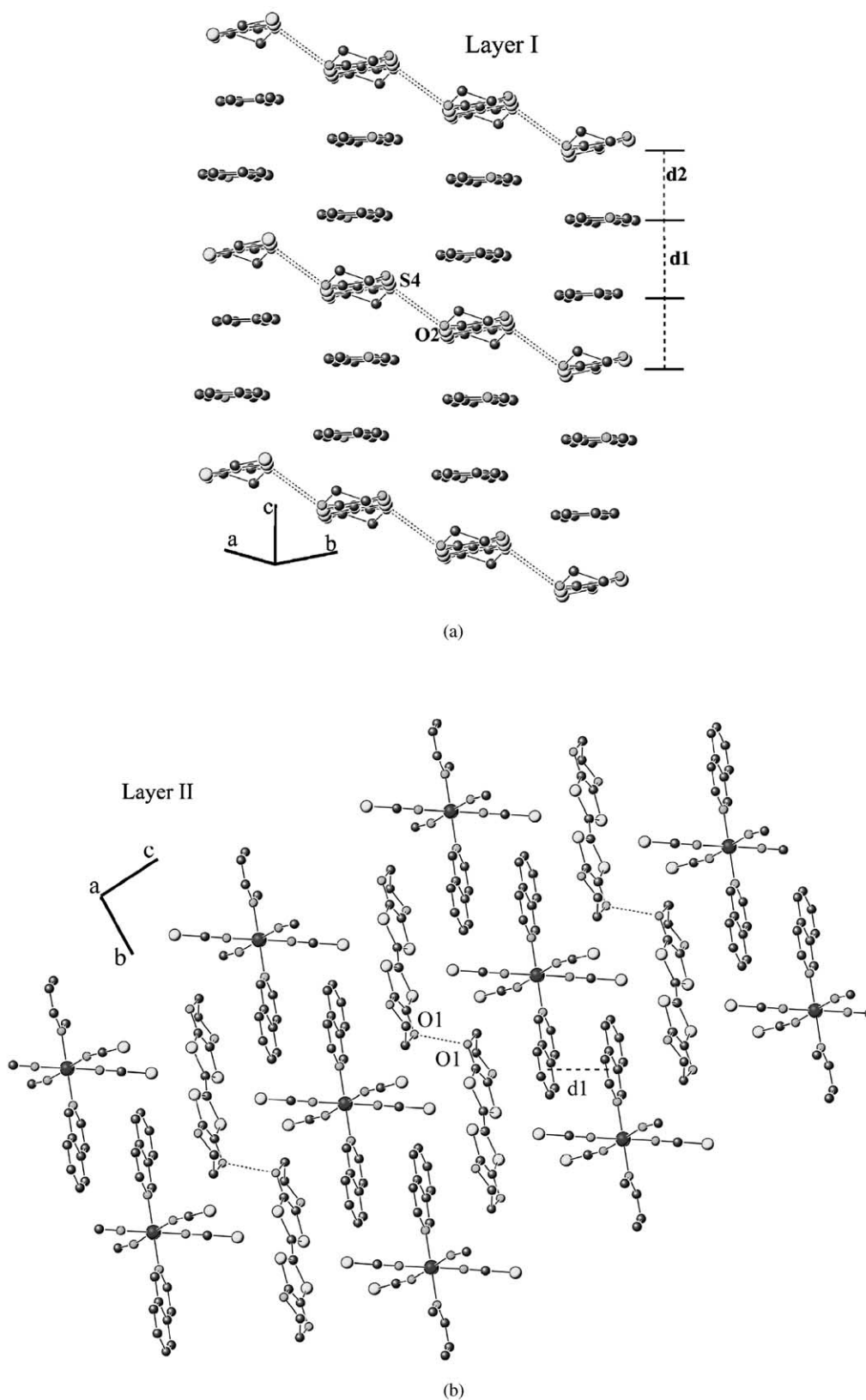
(a)

(b)

FIG. 2. (a) Projection of the organic layer (**I**) showing the π stacking between the isoquinoline ligands and the BO molecules, $O2 \cdots S4 = 3.325(3)$ [3.356(5)] Å, $d1 = 3.549(4)$ [3.532(6)] Å, $d2 = 3.642(5)$ [3.637(6)] Å; (b) projection of the layer (**II**) onto the bc plane showing the mixed chain of anion and donor; $O1 \cdots O1 = 3.187(2)$ [3.194(8)] Å.
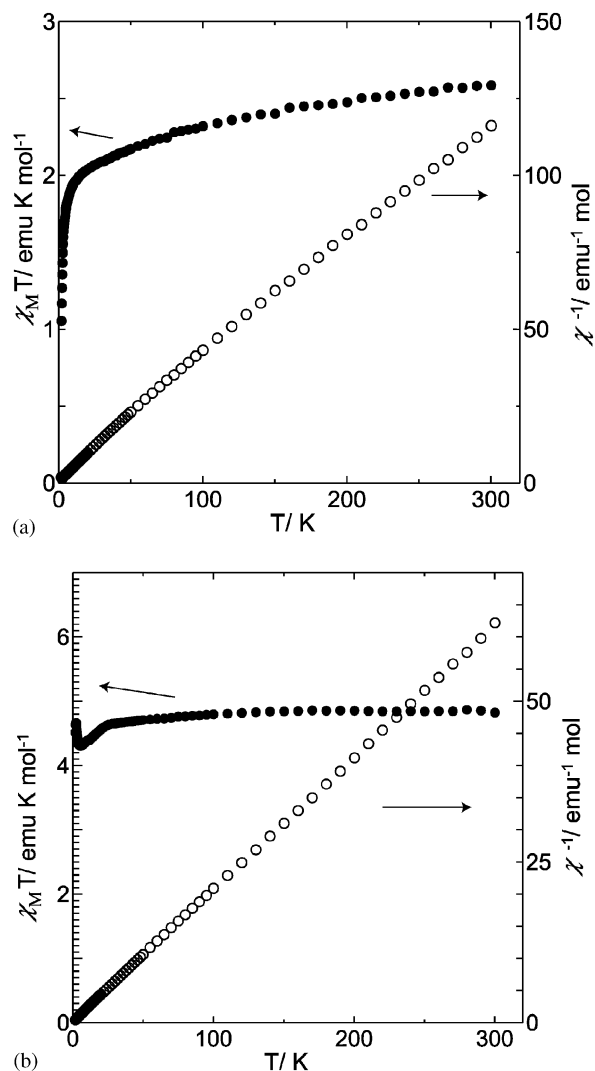
the anions are derived by lattice translation and therefore they have the same orientation preventing the occurrence of such weak canted ferromagnetism. From these three points, it appears clearly that for structural reasons the antiferromagnetic interactions are dominant in our BO salts. Actually, in the title compounds, anion-anion interactions are present in the form of $\pi \cdots \pi$ stacking between nearest neighbor isoquinoline ligands which enforces the spin configuration to be antiparallel in general (10c).

CONCLUSION

Two new charge transfer salts $(BO)[M(isoq)_2(NCS)_4]$ with $M = Cr^{III}$ (1) and Fe^{III} (2) were prepared and structurally and magnetically characterized. These two compounds are isostructural to each other with the 1:1 stoichiometry. The crystal structure contains mixed chains of organic and inorganic units with alternate anion ($S = \frac{3}{2}$ or $S = \frac{5}{2}$) and donor ($S = \frac{1}{2}$) spins. Unlike BEDT–TTF and BDHTTP (11) salts with the same thiocyanato-complex anions and same stoichiometry, the title compounds did not undergo bulk ferri or ferromagnetic ordering. This point was explained by a comparison of the crystal structure of the title compounds with those of BEDT–TTF and BDH–TTP salts to point out the subtle influence of the solid-state arrangements and interactions between molecules on the magnetic properties.

Supplementary Material

Plots of the magnetizations as a function of the field at 2 K for both compounds (1) and (2).

FIG. 3. Temperature dependence of $\chi_M T$ ($\bullet$) and χ_M^{-1} ($\circ$) for non-oriented samples, measured with an applied field of 10 mT. (a) Compound (1) $C = 2.59$ emu K mol^{-1}, (b) compound (2) $C = 4.82$ emu K mol^{-1}.

$S_{anion} \cdots S_{donor}$ contacts ≤ 3.60 Å are present in the BEDT–TTF (the shortest distance is 3.481 Å) and BDH-TTP (the shortest distance is 3.264 Å) containing salts while the corresponding shortest contact in BO salt is 3.714 [3.717] Å; (ii) As shown in Fig. 1b, short S4$\cdots$O2 contacts are observed between BO units of adjacent layers in the title compounds while this kind of interlayer contacts are not present in the other salts; finally, (iii) the three salts crystallize in different space groups, $P2_1/c$, $C2/c$ and $P\bar{1}$, respectively, for BEDT–TTF-, BDH–TTP- and BO-containing salts. As a consequence, in the layer of the BDH–TTP salt, neighboring anions are deduced by c-glide plane and do not have the same orientation which yields a canting angle between the anion spins giving rise to a weak canted bulk ferromagnetism (11). However, in the BO salt,

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