Crystal Growth and Physical Properties of Antiferromagnetic Molecule: *trans*-dibromotetrakis (acetonitrile) Chromium (III) Tribromide, [CrBr₂(NCCH₃)₄]Br₃

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Abstract

The synthesis, crystal structure determination, magnetic properties, and bonding interaction analysis of a novel 3d transition metal complex, [CrBr₂(NCCH₃)₄]Br₃ is reported. Single crystal X-ray diffraction results show that $[CrBr_2(NCCH_3)_4]Br_3$ crystallizes in the space group of C2/m(No. 12) with a symmetric tribromide anion and the powder X-ray diffraction results show the high purity of the material specimen. The X-ray photoelectron studies with a combination of magnetic measurements demonstrate Cr adopts the 3+ oxidation state. Based on the Curie-Weiss analysis of magnetic susceptibility data, it can be concluded that the Neel temperature is around 2.2 K and the effective moment (μ_{eff}) of Cr³⁺ in [CrBr₂(NCCH₃)₄]Br₃ is ~3.8 μ_{B} , which agrees with the theoretical value for Cr^{3+} . The dc magnetic susceptibility of the molecule shows a broad maximum at ~ 2.3 K, which is consistent with the theoretical Neel temperature. The maximum temperature, however, shows no clear frequency dependence. Combining with the observed upturn in heat capacity below 2.3 K and corresponding field dependence, we speculate the lowtemperature magnetic feature of a broad transition in [CrBr₂(NCCH₃)₄]Br₃ could originate from a crossover from a high spin to a low spin for the split d orbit level low lying states rather than a short-range ordering solely; this is also supported by the molecular orbits diagram obtained from theoretical calculations.

Introduction:

Molecule based magnets are intriguing among materials community due to their various unique magnetic properties(Miller, 2014; Miller & Gatteschi, 2011). There are two categories of molecule-based magnets: single molecule magnet (SMM) that shows superparamagnetic behaviors at molecular scale(Guo et al., 2018) and the conventional molecule-based magnets which usually hosts the properties such as transparency, electrical insulation and photoresponsiveness (Mudiyanselage et al., 2020; Gatteschi, 1996). The magnetism arising from molecular systems differentiates from conventional condensed matter magnetic materials because the chemistry associated with molecular magnetism can be used for detailed analysis of magnetic behavior in homogeneous materials (Baker et al., 2012). As a result, the theoretical assessments can be testified without considering the sample inhomogeneity, which will help to understand exotic quantum mechanism behind magnetism deeper, for example quantum tunneling of magnetizations in molecules such as manganese clusters (Thomas et al., 1996; Wernsdorfer et al., 2002) and iron clusters (Sangregorio et al., 1997) and spin frustration systems (Schnack, 2010) leading to spin ice (Bramwell & Gingras, 2001) and spin liquid (Shimizu et al., 2016). Furthermore, molecules allow chemical control of the various structure types by changing ligands with respect to conventional magnets. This opens the opportunity to develop novel materials with various emergent phenomena which are not observed in classical conventional magnets (Miller & Gatteschi, 2011). The discovery of first organic based ferromagnet $[Fe(C_5Me_5)_2][TCNE]$ (TCNE = tetracyanoethylene) as a zero dimensional magnetic material is such a milestone (Miller et al., 1987).

On the other hand, spin-dominated quantum materials, including ferromagnetic and antiferromagnetic spintronics, magnetic topological materials, atomically thin layered materials have attracted a lot of interest because such materials are critical in quantum technological applications (Tokura *et al.*, 2017). For example, chromium in CrI₃ and CrGeTe₃ share the same valence state of Cr^{3+} with the d³ electronic configuration (Xu *et al.*, 2018). The magnetism in these compounds originates from the super exchange interactions between Cr^{3+} through the I⁻ or Te²⁻ ligands. Therefore, understanding the relationship among structures, electronic, and magnetic properties is very important to uncover novel materials with exciting physical properties.

The first-row transition metal organo-nitrile complexes have been synthesized decades ago. One reason that inorganic chemists were interested in these compounds is due to their potential application as non-aqueous source of metal ion synthons in development of other novel materials in various fields (Nortia et al., 1984; Getsis & Mudring, 2008; Nelson et al., 2007; Henriques et al., 1998). The focus on the transition metal halide acetonitrile complexes were increased when it was discovered that compounds like divalent NiX₂·xCH₃CN are showing catalytic properties towards diolefin polymerization (Getsis & Mudring, 2008; Zhao et al., 1996). However, due to the low thermal stability and the hygroscopic nature of these compounds, only a few compounds have been completely characterized structurally. Most of these compounds have been investigated using spectroscopic tools (Nortia et al., 1984). According to our knowledge, comprehensive magnetic studies done on these complexes are scarce in the literature. However, these complexes can be viewed as an interesting group of magnetic molecules in the sense of possible super exchange interactions via halide ligands similar to what was observed in the CrI₃ and CrGeTe₃ mentioned above. The inherent simplicity of these molecules in contrast to the large clusters, or the solid-state compounds like CrI3 and CrGeTe3 would be an ideal system to understand the magnetic behaviors, especially underlying exchange interactions.

Therefore, in this study we aimed to understand the magnetic behaviors of the Cr^{3+} ion in a coordinated environment of bromide and acetonitrile as ligands expecting the super exchange interactions through bromide ligands. Only reported bromide compound in this family is the $[VBr_2(NCCH_3)_4][Br_3]$ and no magnetic studies have been reported on this compound (Cotton *et al.*, 1986). Accordingly, herein, the synthesis, complete structural analysis and magnetic properties of the novel $[CrBr_2(NCCH_3)_4][Br_3]$ complex through experimental and theoretical assessments are presented to clarify the intrinsic interplay of the electrons and spin.

Experimental Parts

Synthesis: The compound [CrBr₂(NCCH₃)₄]Br₃ was first discovered during a reaction between pure phase NaCrS₂ solid and Br₂ solution in acetonitrile. Purchased liquid Br₂ (99.8%, Sigma Aldrich) was dissolved in acetonitrile (Emsure, Sigma Aldrich) to prepare 0.6M Br₂ solution. 0.3 mmol (40.4 mg) of NaCrS₂ (crystalline powder, synthesis described below) was added to 6 mmol (10.0ml of 0.6 M) of Br₂ and stirred at 50 rpm for 24 hours before it was filtered and separated from residual solid. The filtrate could slowly evaporate under ambient conditions over a period of one week and the X-ray quality dark green crystals were obtained. The crystals filtered and washed with acetonitrile were stable in air and moisture and used to do the further investigations on physical properties.

The precursor NaCrS₂ was synthesized by a novel solid-state synthesis route. Elemental sodium pieces (99.95% (metal basis), Alfa Aesar), chromium powder (-325 mesh, 99% (metals basis), Alfa Aesar), sulfur (99.9995%, Alfa Aesar) in the molar ratio 1.2:1:2 containing 200 mg in total was weighed, pressed into a pellet inside argon filled glovebox. The pellet was transferred to an aluminum crucible where it was sealed into evacuated silica tube (<10⁻⁵ Torr). The sealed tube was heated up to 700 °C at the speed of 20°C/hr and annealed for 48 hrs, followed by furnace cooling to room temperature yielding pure phase NaCrS₂.

Phase Analysis: The synthesized sample was examined by Philips XPERT powder X-ray diffractometer using Cu K α radiation (λ =1.5406 Å, Graphite monochromator) for the phase identification and purity verification. Data collection was done over the range of Bragg angle (2 θ) from 5 to 90° for 9.5 hrs. Phase identification and lattice parameters were analyzed using the LeBail fitting using Fullprof Software (Le Bail *et al.*, 1988; Dinnebier & Billinge, 2008).

Structure Determination: X-ray quality single crystals were protected by glycerol and mounted on a Kapton loop to conduct the single crystal X-ray diffraction (SCXRD) experiment. Crystals were measured at room temperature in a Bruker Apex II diffractometer with Mo radiation ($\lambda_{K\alpha} = 0.71073$ Å). Experiment was done with an exposure time of 10 s per frame and a scanning 20 width of 0.5°. Direct method and full matrix least-squares on F² model with the SHELXTL package was used for the structure refinement. The anisotropic thermal parameters were refined for all non-hydrogen atoms in SHELXTL. The hydrogen atoms attached to carbon atoms were positioned in the refinement model as C-H = 0.96 Å with fixed thermal parameter;

 $U_{iso}(H) = 1.5U_{eq}(C)$ (Lu *et al.*, 2018; Sheldrick, 2015). The crystal structure were plotted using VESTA software (Momma & Izumi, 2008).

X-Ray Photoelectron Spectroscopy Measurements: The ScientaOmicron ESCA 2SR X-ray Photoelectron Spectroscope System which is equipped with a Flood Source Charge Neutralizer was used to carry out the XPS measurements of the sample. Sample was mounted on the carbon tape and pumped in the preparation chamber more than 8 hours before the analysis. A Mono Al K α x-ray source (1486.6 eV) at the power of 450W, and a pressure below 5×10-9mBarr was maintained in the analysis chamber. The survey scan and all elemental region scans were processed with Casa XPS software. All spectra were calibrated with C1s peak at 284.8 eV. Core level XPS spectra were deconvoluted to obtain chemical state information.

Molecular orbital calculations: Molecular orbital diagrams were generated based on the semiempirical extended Huckel tight binding (EHTB) methods using the CAESAR packages to estimate the chemical bond influence on atomic interactions. The parameters set used in the calculation is given in the **Table 1** (Hoffmann, 1963; Mudiyanselage *et al.*, 2020).

Table 1: Parameters used in the molecular orbital calculation of $[CrBr_2(NCCH_3)_4][Br_3]$ using CAESER software (version. 2.0, PrimeColor Software, Raleigh, NC, USA) with the extended-Hückel-tight-binding method.

Atom	AO	H _{ii} (eV)	ζ1	C 1	ζ2	С2
Cr	S	-8.66	1.700	1.000		
	р	-5.24	1.700	1.000		
	d	-11.22	4.950	0.506	1.800	0.675
Br	S	-22.07	2.588	1.000		
	р	-13.10	2.131	1.000		
Ν	S	-26.00	1.950	1.000		
	р	-13.40	1.950	1.000		
С	S	-21.40	1.625	1.000		
	р	-11.40	1.625	1.000		
Н	S	-13.60	1.300	1.000		

 H_{ii} = -VSIP (valence-state ionization potential [eV]). The double-zeta (for Cr 3*d*) or single-zeta (for the remaining orbitals) Slater type orbitals (STO's) are used;

$$\chi_{\mu}(r, \theta, \phi) \propto r^{(n-1)} \exp(-\zeta r) Y(\theta \phi) \text{ (single-zeta STO)}$$

 $\chi_{\mu}(r, \theta, \phi) \propto r^{(n-1)} [c_1 \exp(-\zeta_1 r) + c_2 \exp(-\zeta_2 rI)] Y(\theta, \phi)$ (double-zeta STO)

 c_1 and c_2 correspond to 1 and 0 in single-zeta STO, and c_1 and c_2 in double-zeta STO, respectively.

Physical Property Measurements: The Quantum Design Dynacool Physical Property Measurement System (PPMS) was used to measure the magnetic properties of both DC and AC methods on the sample packed in a plastic capsule. The instrument operates over a temperature range of 1.8-300 K and field up to 90 kOe. The magnetic susceptibility is defined as $\chi = M/H$. M is the magnetization in units of emu and H is the applied magnetic field. Temperature dependence of dc magnetic susceptibility (χ) of polycrystalline sample of [CrBr₂(NCCH₃)₄]Br₃ was measured with external magnetic field ranging from 50 Oe to 90 kOe.

A standard relaxation calorimetry method was used to measure heat capacity and the data were collected in zero magnetic field between 1.8 K and 50 K and under magnetic fields of 10 kOe, 30 kOe, 50 kOe and 70 kOe at the temperature range of 1.8 K – 15 K. All of the measurements were performed on polycrystalline sample of $[CrBr_2(NCCH_3)_4]Br_3$ and the measurements were conducted on different specimens to confirm the reproducibility.

Results and Discussion

Phase Analysis: The PXRD pattern refined using LeBail method for $[CrBr_2(NCCH_3)_4]Br_3$ is shown in **Figure 1**. The red points and black solid lines indicate the experimental and calculated intensities, respectively. According to PXRD analysis of the compound, it is clear that the synthesis attempt has yielded the phase pure $[CrBr_2(NCCH_3)_4]Br_3$ compound. Furthermore, this has confirmed that the compound crystallizes in a monoclinic unit cell with the space group C 2/m (No. 12) and refined lattice parameters are a = 14.70879(1) Å, b = 10.33470(1) Å, and c = 6.31131(1) Å ($\chi^2 = 1.61$).



Figure 1. Powder diffraction pattern of $[CrBr_2(NCCH_3)_4][Br_3]$. The red points, black solid line and blue solid line represent experimental data (I_{obs}), the calculated LeBail refinement (I_{cal}) and the difference between calculated and observed intensities ($I_{obs} - I_{cal}$), respectively. The vertical bars mark the expected Bragg positions.

Crystal Structure Determination: Single Crystal X-Ray Diffraction technique was used to determine the molecular structure of the complex and the results including atomic positions, site occupancies, and isotropic thermal displacements for all atoms are summarized in **Tables 2 and 3**. Anisotropic thermal displacements details are given in **SI**. The molecule adopts a monoclinic structure in space group C 2/m (No. 12) with a similar structure type of isoelectronic species

[VBr₂(NCCH₃)₄][Br₃](Cotton *et al.*, 1986), [MoI₂(NCCH₃)₄][I₃] and [WI₂(NCCH₃)₄][I₃].(Leigh et al., 2002) The overall crystal packing is built upon the alternating layers of [Cr(NCCH₃)₄Br₂]⁺ cation and the $[Br_3]^-$ anion as shown in Figure 2a. Structural characterization revealed the octahedral cation with four similarly coordinated MeCN and two bromide ligands as shown in Figure 2b and 2c. Unlike the distorted octahedral coordination exhibited in $[Cr^{(III)}(MeCN)_6][BF_4]_3$ (Hatlevik et al., 2004) and $[Cr^{(II)}(MeCN)_4](BF_4)_2]$ (Henriques et al., 1998), this compound shows a regular octahedron which is structurally similar to the isoelectronic [VBr₂(NCCH₃)₄][Br₃] [MoI₂(NCCH₃)₄][I₃] and [WI₂(NCCH₃)₄][I₃]. Substituting the MeCN ligands with halogen ligands may have led to lower steric hindrance resulting nondistorted octahedron. The Cr-N bond for this molecule is 2.022(3) Å which is 0.064 Å shorter than [Cr^(II)(MeCN)₄](BF₄)₂] and 0.023 Å longer than [Cr^(III)(MeCN)₆][BF₄]₃. Detailed bond lengths and angles reported in **Table 4** further support the non-distorted nature of the octahedral coordination of the compound. The shortest Br....H₃C separation is 2.99 Å, which is close to the sum of Van der Waal radii of H and Br (3.05 Å). This indicates that there is no possible hydrogen bonding between cation and anion in the crystal lattice similar to observed behavior of F....H₃C in [Cr^(III)(MeCN)₆][BF₄]₃ (Hatlevik *et al.*, 2004).

Empirical formula	$[Cr(NCCH_3)_4Br_2][Br_3]$
Formula weight (g/mol)	615.77
Temperature (K)	296.15
Crystal system	Monoclinic
Space group; Z	C 2/ <i>m</i> ; 2
a(Å)	14.700(7)
b(Å)	10.319(5)
c(Å)	6.308(3)
α(°)	90
β(°)	103.68(1)
γ(°)	90
Volume (Å ³)	929.8(8)
Extinction coefficient	None
θ range (°)	2.435 to 35.007
No. reflections; Rint	2081; 0.0471
No. independent reflections	2081
No. parameters	50
$R_1: \omega R_2 (I > 2\delta(I))$	0.0464: 0.1055
R indices (all data) R_1 : ωR_2	0.0811: 0.1194
Goodness-of-fit on F ²	1.017

Table 2. Single crystal refinement data for the compound [Cr(NCCH₃)₄Br₂][Br₃].

Atom	Wyck.	x	уу	Ζ	Occ.	Ueq
Cr1	2 <i>d</i>	0	1/2	1/2	1	0.0246(2)
Br1	4 <i>i</i>	0.3680(1)	0	0.1817(1)	1	0.0428(2)
Br2	2 <i>c</i>	0	0	1/2	1	0.0468(2)
Br3	4 <i>i</i>	0.1738(2)	0	0.6857(1)	1	0.0641(2)
N1	8 <i>j</i>	0.0644(1)	0.3631(1)	0.3584(1)	1	0.0362(5)
C1	8 <i>j</i>	0.1024(1)	0.2921(1)	0.2763(2)	1	0.0394(7)
C2	8 <i>j</i>	0.1525(1)	0.2011(1)	0.1705(2)	1	0.0694(14)
H1	8 <i>j</i>	0.19866	0.24668	0.11409	1	0.104
H2	8j	0.18291	0.13747	0.27441	1	0.104
Н3	8j	0.10925	0.15888	0.05293	1	0.104

Table 3. Atomic coordinates and equivalent isotropic displacement parameters of the compound $[Cr(NCCH_3)_4Br_2][Br_3]$. (U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor (Å²)).



Figure 2. Crystal structure of $[CrBr_2(NCCH_3)_4][Br_3]$ showing (*a*) anion and cation arrangement along *ab* plane (*b*) Labeled octahedral ligand coordination around the Cr atom and tribromide anion (*c*) The Cr-cluster in each unit cell. (*d*) Image of the crystal with the size ~0.5mm (*e*) Cr-Cr framework showing bond lengths of possible smallest triangle.

The compound is formed with tribromide anion to make the charge balance, which is not commonly observed in transition metal complexes unlike its triiodide counterpart (Cavallo *et al.*, 2016; Leigh *et al.*, 2002) The tribromide ion is less stable in aqueous solutions (Cotton *et al.*, 1986). Closer look at the structural parameters show that the tribromide anion is linear with symmetric bond length of 2.5461(7) Å which is a specific feature observed for the tribromide anion in this molecule (Therald Moeller, 1961). This has been also characteristic in the $[VBr_2(NCCH_3)_4][Br_3]$ molecule, which is the only reported completely symmetric $[Br_3]^-$ ion (Cotton *et al.*, 1986). Most of previously reported compounds show asymmetric $[Br_3]^-$ with different Br-Br bond distances ranging from 2.38 to 2.70 Å as confirmed by spectroscopic studies and theoretical calculations (Caminiti *et al.*, 1997; Burns & Renner, 1991).

-	Distance/(Å)	Bo	Bond Angle/(°)		
Cr1-Br1	2.440(1)	N1-Cr1-N1	91.38(16)		
Cr1-N1	2.022(3)	N1-Cr1-N1	88.62(16)		
N1-C1	1.120(5)	Br1-Cr1-N1	90.05(8)		
C1-C2	1.450(7)	Br1-Cr1-N1	89.95(8)		
		N1-Cr1-N1	180.00(0)		
		Br1-Cr1-Br1	180.00(0)		
		Cr1-N1-C1	176.5(3)		
		N1-C1-C2	179.4(4)		
Br2-Br3	2.546(1)	Br3-Br2-Br3	180.00(0)		

Table 4. Interatomic distances and angles for $[CrBr_2(NCCH_3)_4][Br_3]$. Refer to the Figure 1*b* for labeled atoms

XPS analysis of [CrBr₂(NCCH₃)4][Br₃]: The formal oxidation state of the central chromium atom and the chemical status of N and Br atoms were supported by the XPS analysis. The spectrum shown in **Figure 3***a* for Cr region shows that the complex has only one Cr species. The peaks 577.3 eV (Cr 2*p*_{3/2}) and 586.88 (Cr 2*p*_{1/2}) are representing the bulk material. The binding energy value 577.3 eV for Cr 2*p*_{3/2} component is in the range of values for Cr³⁺ species. More specifically, Cr 2*p*_{3/2} for Cr³⁺ in CrBr₃, CrI₃, Cr₂O₃, CrCl₃ and CrF₃ are 576.4, 576.9, 577.0, 577.6, 580.5 eV respectively (Carver *et al.*, 1972). However the slight change in the binding energy of [CrBr₂(NCCH₃)₄][Br₃] is due to the alterations in the chemical environment influenced by the MeCN ligands. Compared to the CrBr₃ species, the binding energy has been shifted to a higher value in [CrBr₂(NCCH₃)₄][Br₃] representing a more oxidized Cr species. Upon substitution of N atom which is more electronegative than Br in CrBr₃, has led to electron density changes of the valence shell of Cr in [CrBr₂(NCCH₃)₄][Br₃] corresponding to the increased core level binding energies observed in the spectrum.



Figure 3. XPS spectrum of $[CrBr_2(NCCH_3)_4][Br_3]$ with its simulated peak fitting of *a*) Cr-2*p b*) Br-3*d* (Inset: N 1*s* fitting).

The XPS analysis of the Br region confirms that there are two Br species present in the complex as shown in the **Figure 3b**. The Br 3*d* spectrum is characteristic with a doublet peak due to the spin orbital coupling with ΔE of 1.05 eV. For clarity $3d_{5/2}$ peak will be used to explain the results as it has the higher intensity among two components. The lower energy peak 67.58 eV correspond to Br⁻ ligand attached to the Cr center while the higher energy peak at 68.91 eV can be assigned to the Br from tribromide anion ([Br₃]⁻). The bromine atom in tribromide anion is more electropositive than the Br- as the negative charge in the [Br₃]⁻ delocalized over 3 atoms. As a result of this charge density dilution in [Br₃]⁻ compared to Br⁻, the peak for [Br₃]⁻ appeared about 1.5 eV higher than Br⁻ (Rui Mu *et al.*, 2020). The inset of **Figure 3***b* shows the spectrum for N region. Observation of one N species in the complex further supports the crystallographic determination of identical N coordination of four acetonitrile ligands.

Physical Properties of [CrBr₂(NCCH₃)₄][Br₃]: The results of both field-cooled (FC) and zero-field-cooled (ZFC) χ vs T for different external fields are shown in **Figure 4***a*. Magnetic susceptibility values at higher temperatures at different external fields measured are almost

identical. On cooling down the sample, its magnetic susceptibility increases, following the Curie-Weiss law. An analysis of the magnetic susceptibility was modeled by using $\chi = \chi_0 + \frac{c}{T - \theta_{CW}}$ (shown in Figure 4b). Here, χ , χ_0 , C, and θ_{CW} represent magnetic susceptibility, temperature independent contribution to the susceptibility, Curie constant, and the Curie-Weiss temperature, respectively. The effective moment, μ_{eff} , fitted in the high-temperature range (300–100 K) is 3.8 μ_B at 10 kOe. This is in agreement with the theoretical spin-only μ_{eff} value (3.87 μ_B) for an isolated Cr(III) ion with a d^3 configuration calculated by $\mu_{eff} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons. The fitted Curie–Weiss temperature is -2.3 K where the negative sign indicates the antiferromagnetic exchange interaction of the spins in the compound. Inset in the Figure 4a shows the low temperature behavior of the magnetic susceptibility. A broad maximum is observed at ~2.3 K with no clear difference between the ZFC and FC data. This feature disappears at higher applied field above approximately 10 kOe. In order to further investigate any possibility of short-range magnetic interactions in the material, the ac magnetic susceptibility measurements were done and shown in the SI (Figure SI-1). With one order of magnitude increase of measurement frequency, there is no clear change of maximum temperature within our experimental resolution. This is inconsistent with a short range, spin glass scenario, where compounds typically show spin freezing temperature increases with the increasing exciting frequency.



Figure 4. *a*) Magnetic susceptibility versus temperature measured in zero field cooled (ZFC-open circles) and field cooled (FC- filled circles) at fields 50, 100, 1000, 10k, 30k, and 90k Oe. **Inset:** showing magnetic susceptibility curves at low temperature from 1.8 K-10 K. *b*) Magnetic

susceptibility versus temperature at 10 kOe showing Curie-Weiss fitting parameters, **Inset:** Magnetization vs applied field up to 90 kOe at 1.8 K.

We also carried out field-dependent magnetization measurement at 1.8 K, shown in **Figure 4***b* (**Inset**). According to the isothermal magnetization curve, shown in **Figure 4***b*, the extended linear trend at lower fields indicate a deviation from the simple Brillouin function in $[CrBr_2(NCCH_3)_4][Br_3]$. This is probably associated with the broad maximum observed in the temperature dependent magnetization which will be discussed in more details below. The magnetization at higher field then shows a trend to saturate at Ms ~ $2.8\mu_B/Cr$. This is close to the theoretical saturated magnetic moment ($\mu_{sat} = 3\mu B$) for Cr^{3+} .



Figure 5. Temperature-dependent specific heat at various applied magnetic field.

It is thus far clear that the magnetic property of $[CrBr_2(NCCH_3)_4][Br_3]$ does not follow simple paramagnetic Curie-Weiss law for a fixed spin at low temperature. In order to explore possible long-range magnetic ordering, we measured heat capacity down to 1.8 K. In **Figure 5**, we show temperature-dependent specific heat of $[CrBr_2(NCCH_3)_4][Br_3]$ measured at various applied magnetic fields. At zero field, there is an upturn below ~4.5 K, persisting down to at least 1.8 K, without showing a maximum. Firstly, the maximum in specific heat, albeit not observed, is distinctly not at the same temperature compared to the maximum in temperature-dependent magnetization data (2.3 K). Secondly, the size of such upturn on top of diminishing phonon specific heat at low temperature suggest a bulk nature of magnetic contribution. Therefore, the maximum feature observed in temperature-dependent magnetization is likely intrinsic, rather than from minor impurity phases. The broadness of both magnetic susceptibility and specific heat together suggests a cross-over type magnetic behavior. To further test this hypothesis, we measured the specific heat at various magnetic fields. With increasing magnetic fields, the broad maximum gradually moves towards higher temperatures. This is consistent with a Schottky anomaly due to a widening gap from Zeeman splitting (He *et al.*, 2009). By fitting the data (not shown here), we estimate the gap is close to 5 K at zero field. Rather than long-range magnetic ordering, it is possible that the magnetization maximum, as well as the upturn in specific heat, originates from a high-spin to low-spin crossover for the split quasi- t_{2g} level low lying states.

Molecular Orbital (MO) calculation: Each unit cell of $[CrBr_2(NCCH_3)_4][Br_3]$ contains 271 valance electrons in total. Therefore, the MO #136 can be considered as the highest occupied molecular orbital (HOMO) while MO #137 is the lowest unoccupied molecular orbital (LUMO). Both LUMO and HOMO exhibited antibonding features as shown in the **Figure 6.** The localized electron distribution is clearly observed in the molecular orbital diagrams, which is consistent with insulating properties in $[CrBr_2(NCCH_3)_4][Br_3]$. Moreover, the energy difference between HOMO and LUMO orbitals is very small, ~1 meV. The small energy gap requires low energy for spins transiting from HOMO to LUMO orbitals, which also supports the observed magnetization maximus and upturn in specific heat measurements. The cation of $[CrBr_2(NCCH_3)_4][Br_3]$ was found to exist in both HOMO and LUMO, where d_{yz} from Cr, p_y from Br and p_z from N atoms are highly hybridized. No contribution was found from the Br atoms of tribromide anion for HOMO or LUMO orbitals supports that observed magnetization maximum and the upturn in specific heat can be derived from a spin transition for the split t_{2g} level low lying states.



Figure 6. The MO pictures imported from molecular orbital calculations done using CEASER software.

To further understand the electronic interactions in such magnetic molecules, the MO calculations for the isostructural molecules $[VBr_2(NCCH_3)_4][Br_3]$ $[MoI_2(NCCH_3)_4][I_3]$ and $[WI_2(NCCH_3)_4][I_3]$ were also performed. The HOMO and LUMO for all those molecules exhibited similar characters to the $[CrBr_2(NCCH_3)_4][Br_3]$ as described above except for the differences in the energy of the HOMO and the slight differences in their energy gap summarized in **Table 5.** The similarity demonstrates the electronic interactions and hybridization among d-orbit on transition metals and main group elements strongly relate to the crystal structures.

Table 5. Summary of HOMO and LUMO energy levels of isostructural compounds [VBr₂(NCCH₃)₄][Br₃], [CrBr₂(NCCH₃)₄][Br₃], [MoI₂(NCCH₃)₄][I₃] and [WI₂(NCCH₃)₄][I₃].

Compound	# valence e- per unit cell	HOMO / eV	LUMO / eV	Energy gap / meV
[VBr ₂ (NCCH ₃) ₄][Br ₃]	267	#134 -10.5863	#135 -10.5862	0.1
[CrBr ₂ (NCCH ₃) ₄][Br ₃]	271	#136 -10.6224	#137 -10.6220	0.4
[MoI ₂ (NCCH ₃) ₄][I ₃]	271	#136 -10.0388	#137 -10.0380	0.8
[WI ₂ (NCCH ₃) ₄][I ₃]	271	#136 -9.8345	#137 -9.8335	1.0

Conclusion

In this study, we investigate the intrinsic interplay of the electron and spin of Cr^{3+} in a novel 3d transition metal halide acetonitrile complex, $[CrBr_2(NCCH_3)_4][Br_3]$. A comprehensive structural and magnetic property analysis has been conducted via both experimental and theoretical evaluations. It is indicated that the magnetic feature of a broader transition observed for Cr in heat capacity and magnetic measurements are coming from a high spin to low spin crossover. As there were no detailed magnetic studies reported for this family, we believe that the structure-property relationships derived through this study would be important to extend the understanding of magnetic behaviors in molecules with single magnetic ions under different coordination environments.

Supporting Information

Supplementary information, details of author contributions and competing interests; and statements of data are available at <u>https://doi.org/xxx</u> including:

Anisotropic thermal displacement parameters; AC magnetic susceptibility χ' .

Acknowledgements

The work at Rutgers is supported by Beckman Young Investigator award and NSF- DMR-2053287.

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Table of Content



Synopsis:

A novel 3*d* metal transition complex $[CrBr_2(NCCH_3)_4][Br_3]$ is synthesized. A complete structural characterization, a detailed magnetic property study and theoretical evaluations are performed to illustrate the magnetic behaviors of Cr^{3+} in a bromide and acetonitrile ligand coordination environment.