Structure of Cr^{II}F(NCMe)$_2$BF$_4$. Rietveld refinement of a component of a physical mixture of unknown composition†

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The reaction of Cr^{II}(NCMe)$_4$(BF$_4$)$_2$ and [NBu$^n_4$][TCNE] (TCNE = tetracyanoethylene) in CH$_2$Cl$_2$ forms a solid that is a mixture of an amorphous reduced-TCNE containing phase(s) and a crystalline component. Rietveld refinement of the high-resolution, synchrotron X-ray powder pattern enabled the determination of the structure of the crystalline phase to be of Cr^{II}F(NCMe)$_2$BF$_4$ composition and illustrates that this methodology can be used to determine the structure of a crystalline substance of unknown composition in the presence of confounding information from coexisting amorphous material. Cr^{II}F(NCMe)$_2$BF$_4$ exhibits a 1-D chain structure with both μ-F and μ-BF$_4^-$ linkages that forms a nonplanar 6-membered FCrFBFCr ring. Cr^{II}F(NCMe)$_2$BF$_4$ possesses a previously unknown structure type and is a potential source of Cr^{II}F$^+$ for synthesis applications.

Introduction

M^{II}[TCNE]$_2$ (M = Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) magnets have been prepared from the reaction of acetonitrile solvates of M^{II}I$_2$ with TCNE in dichloromethane.[1] Additionally, the reaction of iron,[2] cobalt,[3] and nickel[4] carbonyls with TCNE in CH$_2$Cl$_2$ was also studied; however, magnetically ordering materials were only obtained for iron and nickel. Notably, magnetically ordered materials of Cr^{II}[TCNE]$_2\cdot z$S (S = solvent) composition have yet to be established,[5–7] in contrast to the Prussian blue family of magnets.[8] In an ongoing quest to understand the genesis for the lack of magnetically ordered materials of Cr^{II}[TCNE]$_2\cdot z$S composition, the reaction of Cr(NCMe)$_4$(BF$_4$)$_2$[9a] and [NBu$^n_4$][TCNE][9b] has been investigated, and herein we report the unexpected structure of a reaction byproduct having the unusual composition of Cr^{II}F(NCMe)$_2$BF$_4$ that possesses a previously unknown structure type.

Experimental

Synthesis

A 5 mL CH$_2$Cl$_2$ solution of [NBu$^n_4$][TCNE][9b] (122.4 mg, 0.330 mmol) was added to a Cr(NCMe)$_4$(BF$_4$)$_2$[9a] (128.7 mg, 0.330 mmol) suspension in 10 mL of CH$_2$Cl$_2$. After stirring for 48 h, the dark-brown precipitate was vacuum-filtered, washed with 10 mL of CH$_2$Cl$_2$, and dried in vacuo (yield: 71 mg). IR(KBr): ν_{CH}: 3018(w), 2952(w), 2878(w); ν_{MeCN}: 2318(m), 2291(m); ν_{CN}: 2318(m), 2291(m), 2215(sh), 2161(sh), 2115(s, broad); ν_{BF}: 1157(sh), 1117(s), 1061(s), 993(s); ν_{CrF}: 537(s) cm^{-1}. Note that as discussed below this is not a pure material.

Crystal structure determination†

Preliminary powder X-ray diffraction (PXRD) scans were obtained on a $\theta\angle\theta$ Bruker AXS D8 Advance Diffractometer (2θ of 10 to 60°, step width of 0.02°, counting time of 10 to 20 s per step, voltage of 40 kV , and current of 40 mA) fitted with a Göbel mirror to remove all but the Cu Kα radiation (λ = 1.5418 Å). Samples were sealed in 1.00 mm thin-walled quartz capillaries to prevent moisture absorption/desorption and scans were performed at room temperature (~298 K).

For structure determination, a Si(111) channel-cut monochromator selected a highly collimated incident beam of 0.70048 Å X-rays on the X16C beamline at National Synchrotron Light Source, Brookhaven National Laboratory. The diffracted X-rays were analyzed by a Ge(111) single-reflection crystal and detected using a NaI scintillation counter. The capillary was rotated during data collection for better averaging of the powder pattern data. TOPAS-Academic was used to index, assign the space group and solve the structure by simulated annealing method and subsequent Rietveld refinement.[10]

Results and discussion

The reaction of Cr(NCMe)$_4$(BF$_4$)$_2$ and [NBu$^n_4$][TCNE] in MeCN led to precipitation of a solid that exhibited ν_{CN} absorptions in the range of 2165 ± 50 cm^{-1} indicative of the presence of metal bonded [TCNE]$^{\bullet-}$.[11] Preliminary powder X-ray diffraction (PXRD) scans indicated that the material was crystalline. The crystallinity was unexpected, as all other solvates of the anticipated M^{II}[TCNE]$_2\cdot z$S composition were amorphous, and attempts to grow single crystals were unsuccessful. High-resolution X-ray powder patterns† were collected and the structure of the crystalline phase was determined by direct-space searching method (simulated annealing) and Rietveld refinement (Fig. 1).

The usual methods of crystallography require knowledge of the chemical composition of the sample, and so the solution of this structure involved considerable trial and error. The initial attempt using direct methods (EXPO)[12] did not give a true solution, but it indicated the heaviest concentration of charge (metal atom) at the origin, and the existence of tetrahedral clusters suggestive of BF$_4^-$ from the precursor material. This initial structure was improved by several cycles of simulated annealing using TOPAS-Academic.[10]

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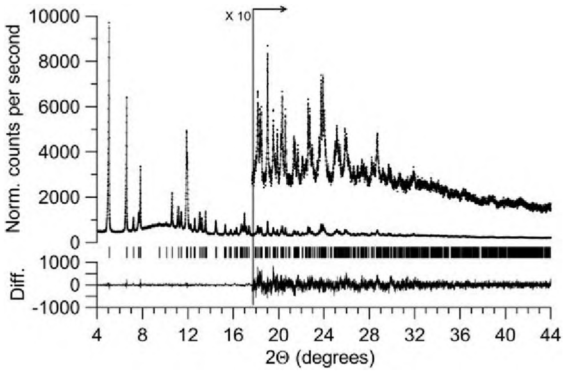

Fig. 1 High-resolution synchrotron powder-diffraction data (dots) and Rietveld fit for the refined structure of $Cr^{II}F(NCMe)_2BF_4$ (solid line). The lower trace is the difference (measured − calculated) plotted on the same vertical scale.

refining the position and orientation of the BF_4^- while adding several C atoms. (Refinements at this stage could not distinguish among C, N, and F.) Further optimization revealed a linear molecule bonded to the Cr, assumed to be acetonitrile (NCMe) from the precursor, and an atom between Cr atoms forming 1-D chains along the *c*-axis. Subsequent Rietveld analysis was performed after replacing the trial C atoms with a rigid body (including H) to represent the NCMe molecule. However, the fit was not satisfactory and clearly the data required a stronger atomic scatterer than the initial guess for the atoms bridging adjacent Cr sites. By refining the occupancy its atomic type was concluded to be fluorine. Identical isotropic-displacement parameters are assigned to the atoms that belong to the same group (*i.e.* BF_4^- and NCMe).

The structure of the crystalline component of the isolated material was determined to be $Cr^{II}F(NCMe)_2BF_4$, and its crystallographic data is summarized in Table 1. The composition of the crystalline phase lacked any form or fragment of TCNE, hence the solid was a mixture of crystalline $Cr^{II}F(NCMe)_2BF_4$ and at least one amorphous component possessing some form or fragment of TCNE. The broad background between 8 and 12° 2θ in the profile suggests the presence of an amorphous component. Attempts to purify, separate, and/or independently prepare and isolate either of the pure components have yet to be successful. Hence, all that can be reported is the structure of $Cr^{II}F(NCMe)_2BF_4$.

The structure consists of an octahedral Cr(II) site bound to two bridging fluorides, two molecules of acetonitrile and two tetrafluoroborate fluorides, Fig. 2. The Cr–N, C–N, and C–C distances are 2.12(2), 1.06(3) and 1.44(3) Å respectively, and the Cr–N–C angle is 164(2)°. This deviation from nonlinearity is unusual, but has been reported previously, *e.g.* 165.6° for $Cr_2(O_2CMe)_4(NCMe)_2$.[13] The Cr–F distances are 1.94(2) and 2.45(2) Å for the bridging and BF_4^- fluorides respectively. The intrachain Cr···Cr separation is 3.628 Å, while the shortest interchain Cr···Cr separation is 8.061 Å.

$Cr^{II}F(NCMe)_2BF_4$ possesses extended, parallel 1-D ···Cr–F–Cr–F··· zigzag chains with 138(1)° Cr–F–Cr angles. In addition to the bridging μ-F, μ-BF_4^- bridges two Cr(II) ions, and both form 6-membered nonplanar CrFCrFBF rings. Bridging Cr–F–Cr linkages are expected to be linear in systems with less than 18 electrons,[14] and the observed significant departure from this is attributed to the structural requirement of μ-BF_4^- that completes the 6-membered CrFCrFBF ring and bends the ···Cr–F–Cr–F··· linkages.

Table 1 Summary of Crystallographic data for $CrF(NCMe)_2BF_4$†

Parameter	$CrF(NCMe)_2BF_4$
Empirical formula	$C_4H_6BCrF_5N_2$
Formula mass/g mol^{-1}	239.92
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	12.2555(5)
b/Å	10.4744(5)
c/Å	7.2559(4)
B/°	83.018(2)
V/Å^3	924.53(8)
Z	4
ρ_{calc}/g cm^{-3}	1.723
T/K	293(2)
λ/Å	0.700486(3)
Angular range	2.000 to 45.000° in steps of 0.005°
$R_{wp}{}^{a,b}$	0.0341
$R_{exp}{}^{b,c}$	0.03016
GOF $(\chi^2)^{1/2} = R_{wp}/R_{exp}$	1.141

[a] $$R_{wp} = \sqrt{\frac{\sum_i w_i(y_i{}^{calc} - y_i{}^{obs})^2}{\sum_i w_i(y_i{}^{obs})^2}}$$

[b] $y_i{}^{calc}$ and $y_i{}^{obs}$ are the calculated and observed intensities at the *i*th point in the profile, normalized to monitor intensity. The weight w_i is $1/\sigma^2$ from counting statistics, with the same normalization factor. N is the number of points in the measured profile.

[c] $$R_{exp} = \sqrt{\frac{N}{\sum_i w_i(y_i{}^{obs})^2}}$$

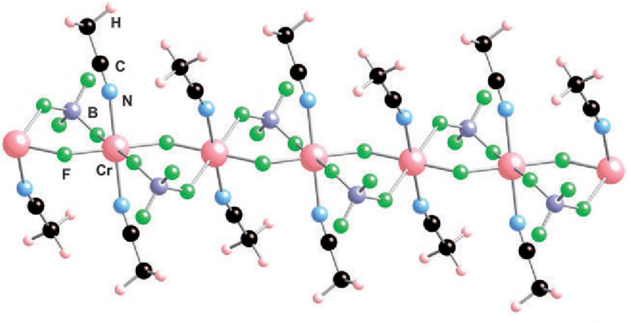

Fig. 2 Structure of $Cr^{II}F(NCMe)_2BF_4$. Bond lengths are 1.94(2) Å for Cr–FCr, 2.12(2) Å for Cr–N, 1.06(3) Å for C–N, 2.45(2) Å for Cr–FB, 1.37(5) Å for B–FCr, and 1.30(5) Å for B–F; angles are 138(1)° for Cr–F–Cr, 164(2)° for Cr–N–C, and 180° (by symmetry) for F–Cr–F.

The source of the bridging fluoride is ascribed to BF_4^-. While not a common fluoride source, fluoride abstraction from BF_4^- has been reported in several circumstances.[14–16] The presence of the fluoride ion is attributed to the dissociation of the BF_4^- in MeCN to give F^- and $BF_3 \cdot MeCN$,[17] and has been observed to result in the formation of a Cr^{III}–F bond and $BF_3 \cdot THF$. Both chelating[18,19] and bridging BF_4^-,[19,20] albeit rare, have also been reported. The observed 2.453 Å Cr–FB bond is comparable to that observed for BF_4^- bridging Co ions (2.405 Å) and shorter than that reported for Cu (2.50–2.69 Å) or

Ag (2.53–3.01 Å) ions. Interestingly, a pair of 6-membered MFMFBF rings have also been observed for M = Cu.[20d,e] Full characterization of $Cr^{II}F(NCMe)_2BF_4$ awaits the availability of a pure material. Antiferromagnetic coupling among the Cr^{II} sites is expected.

Conclusion

In addition to a new composition, the structure of $Cr^{II}F(NCMe)_2BF_4$ represents a new structure type that should be expected to be observed for other divalent first row transition metal ions. This species should be an excellent synthon for $Cr^{II}F^+$; however, a better preparative route needs to be identified.

The techniques of powder diffraction, including direct-space simulation methods and Rietveld refinement are widely seen to be important for the determination of the structure of solids for which single crystals are unavailable. These methods generally require an initial close approximation to the chemical structure of the diffracting material. Here, we have shown that they can be used to discover a chemical composition and structure that is entirely unanticipated. Without taking this step, one might have concluded that Fig. 1 represents the powder X-ray diffraction pattern of a new, crystalline $M^{II}[TCNE]_2$ sulfide *etc.* based on the presence of metal–TCNE bonding inferred from the IR data.

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