Synthesis, characterization, and reactions of tetrakis(nitrile)chromium(II) tetrafluoroborate complexes †

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Reaction of chromium(II) acetate with HBF_4 in nitrile solutions led to air-sensitive, paramagnetic complexes of the general formula $[Cr(NCR)_4][BF_4]_2$ (R = Me, Bu^t or Ph). In contrast to an earlier report of the synthesis of $[Cr(NCMe)_4][BF_4]_2$ by electrochemical methods, these compounds are blue. The crystal structure of $[Cr(NCMe)_4][BF_4]_2$ has been determined. The chromium(II) cation is surrounded by nitrile ligands in a square-planar manner. The BF_4^- counter ions are located at the apical positions of an elongated octahedron. Magnetic susceptibility measurements yielded $\mu_{eff} = 4.9 \mu_B$ at 300 K which is characteristic for a d^4 high-spin complex. The paramagnetic complexes $[Cr(NCR)_4][BF_4]_2$ are easy to prepare and can be used for the high-yield synthesis of several other chromium derivatives in low oxidation states like $[Cr(py)_4][BF_4]_2$, $[Cr(C_5H_5)_2]$, $[Cr(dppe)_2][BF_4]_2$ and $[Cr(NO)(NCMe)_5][BF_4]_2$.

Since their discovery nearly 140 years ago,[1] a large number of transition-metal organonitrile complexes have been prepared and found useful applications. Beyond the interest in the chemistry of co-ordinated nitriles most of the usefulness of these complexes stems from the lability of the nitrile ligands which makes them widely employed starting materials for the synthesis of other complexes,[2a] inorganic materials[2b,c] and catalysts.[2d]

The general synthetic method for the preparation of nitrile complexes is the solvolysis of co-ordinatively or electronically unsaturated transition-metal ions or fragments generated in nitrile solution. Therefore, nitrile co-ordination has allowed the trapping of otherwise unstable intermediates or species. As an example, the exhaustive protonation of the acetato ligands in $Mo_2(O_2CMe)_4$ leads to the labile $[Mo_2(NCMe)_{10}]^{4+}$, a stabilized derivative of the Mo_2^{4+} core.[3] This labile compound has also proven to be a versatile starting material for both the preparation of other complexes of the Mo_2^{4+} core[4] and also for use in catalytic processes like olefin polymerization.[5] Following our interest in the chemistry of Group 6 $[MM']^{4+}$ complexes, these results prompted us to attempt the preparation of nitrile derivatives of the bimetallic chromium-containing $[Cr_2]^{4+}$ and the heteronuclear $[CrMo]^{4+}$ metal core by the similar protonation of $Cr_2(O_2CMe)_4$ and $CrMo(O_2CMe)_4$. The result of these investigations led to recharacterization of the highly reactive $[Cr(NCR)_4(FBF_3)_2]$ complexes, one of which was previously

proposed to be obtained in small amounts from electrochemical reactions but barely characterized.[6] We therefore want to correct these findings and present the correct experimental data for this complex.

Experimental

Materials

The compounds $Cr_2(O_2CMe)_4$[7a] and $CrMo(O_2CMe)_4$[7b] were prepared as reported previously. The nitriles were predried over phosphorus pentaoxide, then distilled from calcium hydride under an atmosphere of dry dinitrogen or argon. They were kept over 3 Å molecular sieves. Tetrafluoroboric acid was obtained from Aldrich as a diethyl ether solution (54%). All manipulations were performed using standard vacuum-line and Schlenk techniques under a dry and oxygen-free atmosphere of argon. Microanalyses were performed at the TUM (Garching) laboratories. Infrared spectra were recorded on a Perkin-Elmer 1650 Series FTIR and Nicolet FT-5DX spectrometer, Raman spectra on a triple Raman spectrometer (Instruments S.A).

Synthesis, analytical and spectral characterization

Complexes 2. The compound $Cr_2(O_2CMe)_4$ **1** (5.0 g) was suspended in a mixture of nitrile (20 cm³) and methylene chloride (40 cm³). The mixture was treated with $HBF_4 \cdot Et_2O$ (10 cm³) which was slowly added with vigorous stirring. The reaction mixture turned deep blue immediately and the orange starting material disappeared within minutes. The solution was stirred for 2 h, and the solvents were removed in oil-pump vacuum. The remaining blue oil was washed several times with diethyl ether and crystallization induced by scratching the wall of the round-bottom flask. The pale blue precipitate was then washed with diethyl ether (20 cm³) and n-pentane (20 cm³), and dried in

oil-pump vacuum. Compounds [Cr(NCMe)$_4$][BF$_4$]$_2$ **2a** and [Cr(NCPh)$_4$][BF$_4$]$_2$ **2b** are pale blue as a powder and deep blue as crystals and [Cr(NCBu^t)$_4$][BF$_4$]$_2$ **2c** is greenish blue (Found: C, 24.7; H, 3.2; N, 14.3. C$_8$H$_{12}$B$_2$CrF$_8$N$_4$ **2a** requires C, 24.7; H, 3.1; N, 14.4. Found: C, 53.0; H, 3.1; N, 8.7. C$_{28}$H$_{20}$B$_2$CrF$_8$N$_4$ **2b** requires C, 52.7; H, 3.2; N, 8.8. Found: C, 43.0; H, 6.6; N, 9.9. C$_{20}$H$_{36}$B$_2$CrF$_8$N$_4$ **2c** requires C, 43.0; H, 6.5; N, 10.0%).

Solid-state ^{1}H and ^{13}C NMR measurements of the paramagnetic samples were recorded on a Bruker MSL 300 spectrometer (high power mode). A 4 mm double-bearing MAS probe head and ZrO$_2$ were used. Chemical shifts are given on a scale with δ(SiMe$_4$) 0. Adamantane was used as a second external standard. NMR (room temperature, 15 kHz): ^{1}H, **2a**, δ 180; **2b**, 6.5; **2c**, −1, 15; ^{13}C: **2a**, δ 500; **2b**, 321, 184, 28; **2c**, 241, 138, 79. The ESR spectra were collected with an X-band Bruker ESP300E spectrometer fitted with an ESR900 liquid-helium flow cryostat (Oxford Instruments), using powder samples of the complexes. At *ca.* 4.5 K the spectra yielded the following values of g_{av}: **2a**, 1.981; **2b**, 1.976; **2c**, 1.977. The UV/VIS spectra were measured under argon and the following absorption data obtained (wavelength in nm; sh = shoulder): **2a** (in MeCN solvent), 616, 412; **2b** (in CH$_2$Cl$_2$ solvent), 598, 446, 418 (sh); **2c** (in NCBu^t solvent), 644, 432, 328. Absorption bands at similar wavelengths are observed for related CrX$_2$-(NCMe)$_2$ complexes.[8]

The complex [Cr(NCMe)$_4$][BF$_4$]$_2$ **2a** and its congeners **2b**, **2c** are not stable in air, both in solution and in the solid state. Exposing a sample of **2a** to pure oxygen leads to a brownish oxygen-containing solid. Addition of water to a solution of **2a** in MeCN leads to a clear solution (replacement of MeCN by H$_2$O, as shown by elemental analysis of the solid recovered after evaporation). Compounds **2a**–**2c** are soluble in their parent nitriles; **2b** is also soluble in CH$_2$Cl$_2$. The molar conductivity of a 10^{-3} mol dm^{-3} solution of **2a** in MeNO$_2$, at room temperature, was Λ$_M$ = 89.5 Ω^{-1} cm^2 mol^{-1}.

'[CrMo(NCMe)$_{10}$][BF$_4$]$_4$'. The compound CrMo(O$_2$CMe)$_4$ (1.0 g) was suspended in a mixture of nitrile (5 cm^3) and methylene chloride (15 cm^3). The mixture was treated with HBF$_4$·Et$_2$O (2 cm^3) which was slowly added under vigorous stirring. The reaction mixture turned red within seconds, then violet, and deep blue after some minutes. It was stirred for 5 h, and then the solvents were removed in oil-pump vacuum. The remaining blue residue was washed several times with diethyl ether and crystallized from an acetonitrile solution layered by a mixture of diethyl ether and *n*-hexane. Dark blue crystals and a pale blue precipitate appeared. The pale blue precipitate was identified as compound **2a** (elemental analysis and IR evidence). The dark blue crystals were examined by X-ray crystallography. The cell constants found for [Mo$_2$(NCMe)$_{10}$][BF$_4$]$_4$ were *a* = 9.587(4), *b* = 22.010(6), *c* = 10.977(3) Å and β = 108.29(4)° [lit.,^{3d} *a* = 9.586(3), *b* = 22.013(7), *c* = 10.975(4) Å and β = 108.26(4)°].

[Cr(py)$_4$][BF$_4$]$_2$ 3. Complex **2b** (200 mg, 0.31 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3). To this blue solution pyridine (5 cm^3) was added *via* syringe. The solution turned pinkish-violet within minutes and was stirred for 30 min. Then the reaction mixture was brought to dryness and the remaining violet powder washed three times with diethyl ether (10 cm^3). Yield: 160 mg (94%) (Found: C, 44.6; H, 3.7; N, 10.2. C$_{20}$H$_{20}$B$_2$CrF$_8$N$_4$ requires C, 44.3; H, 3.7; N, 10.3%). IR (CCl$_4$ mull in KBr discs; ṽ/cm^{-1}): 3119m, 1887m, 1638vs, 1607vs, 1485s, 1448vs, 1215s, 1159s, 1063vs, 677m, 646m, 608m and 523m. In Nujol mull a peak at 768s cm^{-1} was visible.

[Cr(dppe)$_2$][BF$_4$]$_2$ 4. Complex **2b** (400 mg, 0.630 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3). To this blue solution an excess (0.5 g) of 1,2-bis(diphenylphosphino)ethane (dppe) was added. The reaction mixture changed slowly from blue to yellow. After

stirring for 1 h the reaction mixture was evaporated to dryness and washed with toluene (20 cm^3). Then it was extracted with a mixture of CH$_2$Cl$_2$ (10 cm^3) and diethyl ether (10 cm^3). The product was obtained as a yellowish brown powder in 93% yield (555 mg) (Found: C, 65.3; H, 4.8; P, 6.3. C$_{52}$H$_{44}$B$_2$CrF$_8$P$_2$ requires C, 65.6; H, 4.7; P, 6.5%). IR (KBr, ṽ/cm^{-1}): 3057m, 1526m, 1588m, 1485m, 1435s, 1190w, 1161w, 1096vs, 1057vs, 999s, 745s, 692s and 525m.

[Cr(C$_5$H$_5$)$_2$] 5. Complex **2b** (413 mg, 0.647 mmol) was dissolved in thf (20 cm^3) and heated to 40 °C; NaC$_5$H$_5$ (0.25 g, 1.294 mmol) was added. The reaction mixture turned red within minutes. After stirring for 30 min at room temperature the solvent was removed in oil-pump vacuum and the remaining residue extracted with *n*-hexane. The product was isolated as a red air- and moisture-sensitive powder. Yield: 108 mg (92%) (Found: C, 65.8; H, 5.5; Cr, 28.7. C$_{10}$H$_{10}$Cr requires C, 65.9; H, 5.5; Cr, 28.5%).

[Cr(NO)(NCMe)$_5$][BF$_4$]$_2$ 6. Complex **2a** (268 mg, 0.688 mmol) was dissolved in MeCN (10 cm^3). To this blue solution NOBF$_4$ (0.086 g, 0.688 mmol) was added. The reaction mixture turned immediately yellow and then orange within *ca.* 10 min. It was brought to dryness and the orange-yellow residue washed several times with diethyl ether. Yield: 298 mg (94%) (Found: C, 25.8; H, 3.0; N, 17.9. C$_{10}$H$_{15}$B$_2$CrF$_8$N$_6$O requires C, 26.0; H, 3.3; N, 18.2%). IR (KBr, ṽ/cm^{-1}): 2947m, 2332s, 2303s, 1786s, 1642m, 1580m, 1458m, 1422m, 1061vs, 959m and 523m. IR (Nujol, ṽ/cm^{-1}): 1786s, ν(NO). A value of ṽ(NO) = 1796 cm^{-1} was reported for [Cr(NO)(NCMe)$_5$][PF$_6$]$_2$.[10]

X-Ray crystallography

Suitable crystals of compound **2a** were grown by dissolving the blue powder in acetonitrile and layering it with a mixture of *n*-pentane and diethyl ether. After a few days large deep blue crystals were formed. Single-crystal diffraction experiments were conducted using an Imaging Plate Diffraction System (STOE&CIE) rotating anode with a graphite monochromator. The air- and moisture-sensitive blue crystal fragment was mounted in a capillary. Routine unit-cell identification, data-collection procedures, and structure refinement were followed as previously described.[9] Crystallographic parameters and basic information pertaining to data collection and structure refinement are given in Table 1.

CCDC reference number 186/909.

See http://www.rsc.org/suppdata/dt/1998/1293/ for crystallographic files in .cif format.

Magnetic susceptibility measurements

Magnetic susceptibility measurements of complex **2a** were performed in the range 2.2–300 K using a longitudinal Faraday system (Oxford Instruments) with a 7 T superconducting magnet. A polycrystalline sample weighting 2.55 mg was placed in a thin quartz container sealed under an inert atmosphere of argon. The magnetic field used was 2 T and force was measured with a microbalance (Sartorius S3D-V) applying forward and reverse gradients of 5 T m^{-1}. After the experiment the quartz container was measured under the same conditions. The raw results obtained after removal of the sample-holder contribution were then corrected for the diamagnetic contribution, estimated from tabulated Pascal's constants as 1.82 × 10^{-4} emu mol^{-1}.

Results and Discussion

Synthesis

Reaction of Cr$_2$(O$_2$CMe)$_4$ **1** with HBF$_4$·Et$_2$O in the presence of an excess of nitriles leads to the high-yield formation of

$$1 \qquad R = Me\ \mathbf{2a},\ Ph\ \mathbf{2b},\ Bu^t\ \mathbf{2c}$$
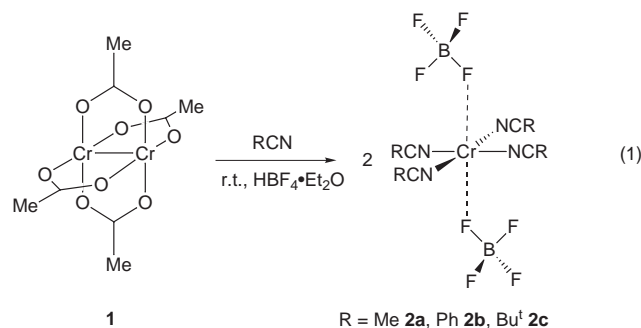
monomeric nitrile complexes **2a**–**2c** according to equation (1). The reaction takes place within minutes and no indications of the formation of any intermediate were obtained as the solution immediately turns blue. This contrasts with protonation of the corresponding molybdenum complex $Mo_2(O_2CMe)_4$ which involves the formation of a red and a violet intermediate $[Mo_2(O_2CMe)_2(NCMe)_6][BF_4]_2$ and $[Mo_2(O_2CMe)(NCMe)_8]$-$[BF_4]_3$, respectively.[3,4a]

In the case of the heterobimetallic congener, CrMo-$(O_2CMe)_4$, reaction with $HBF_4 \cdot Et_2O$ in the presence of acetonitrile leads to the formation of a mixture of complex **2a** and $[Mo_2(NCMe)_{10}][BF_4]_4$ identified by unit-cell determination of the isolated crystals (see Experimental section). In this case a change to red, violet and finally blue can be observed. However, these changes proceed significantly quicker than in the case of $Mo_2(O_2CMe)_4$ as starting material. These observations and results can be understood, considering the weaker Cr≡Cr and Cr≡Mo quadruple bonds in comparison to the stronger Mo≡Mo bond.[11]

All three nitrile derivatives **2a**–**2c** are blue, extremely air- and moisture-sensitive complexes, but can be readily prepared in large quantities and good yields. In an earlier paper **2a** was described as a pink complex isolated from electrochemical experiments.[6] However, the structural characterization and the elemental analysis of the blue crystals of **2a** provide a definitive identification of the complex as $[Cr(NCMe)_4(FBF_3)_2]$. In our experiments we never observed compounds of pinkish color, including the decomposition products of **2a** with pure O_2, degassed water and in moist air which are all greenish brown.

Structural examinations

In the crystal structure of complex **2a** the geometry around the metal is highly distorted octahedral with the acetonitrile ligands arranged in a square-planar fashion. The apical positions are occupied by fluorine atoms of the BF_4^- counter ions. Bond angles and distances are summarized in Table 2, and a PLATON[12] drawing of **2a** is given in Fig. 1. The Cr–N bond distances of 206.9(2) and 206.3(2) pm are similar to those found for polymeric $CrBr_2(NCMe)_2$ [206.6(4) pm][8b] but comparatively longer than those reported for the dications *trans*-$[Cr(NCR)_2(dmpe)_2]^{2+}$ (R = Me or Et) which are in the range between 190.6(6) and 199.4(6) pm.[13a] The Cr–N bond distances in $[Cr(py)_4(FPF_5)_2]$ are 211.3(3) and 209.5(2) pm,[13b] only slightly longer than in compound **2a**. The N–Cr–N angles are very close to 90° showing almost no distortion to a square-planar geometry of the $Cr(NCMe)_4$ fragment on the equatorial plane. The apical Cr–F bond distances are *ca.* 241 pm. A combination of the ionic radii of Cr^{2+} and F^- would sum to *ca.* 215 pm, considerably shorter than the observed bond distances. In the related pyridine complex $[Cr(py)_4(FPF_5)_2]$ the Cr···F distances are similar [244.9(5) pm]. In the chromium(III) complex *trans*-$[Cr(py)_4F_2][PF_6]$ the Cr–F bond distance is, as expected, considerably shorter [185.3(2) pm].[13b] Nevertheless, it should be noted that the Cr–F bond distance in CrF_2 is of the same magnitude as in **2a**.[14] A lengthening of the F–B bond to the coordinating fluorine atom, however, cannot be observed in the
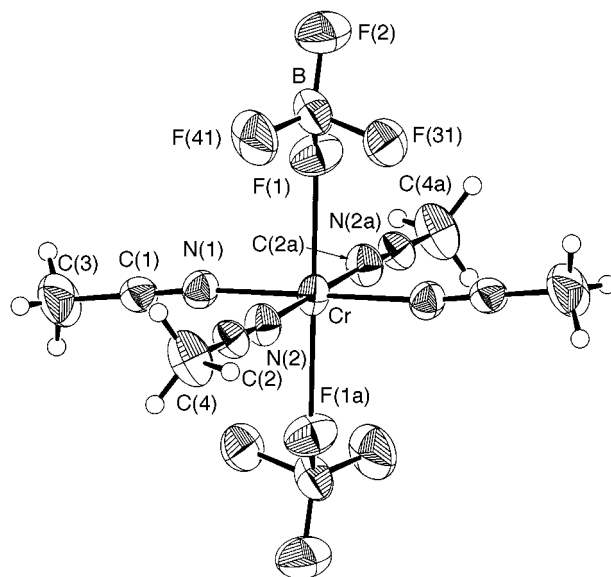

Fig. 1 A PLATON drawing of molecule **2a**. Thermal ellipsoids are shown at 50% probability level

Table 1 Crystal and structure refinement data for $[Cr(NCMe)_4][BF_4]_2$ **2a**

Empirical formula	$C_8H_{12}B_2CrF_8N_4$
M	389.81
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
a/pm	1012.23(4)
b/pm	1310.66(6)
c/pm	1281.94(5)
U/pm³	1700.7(1) × 10⁶
Z	4
D_c/g cm⁻³	1.522
λ/pm	71.073
T/K	153(1)
No. reflections collected	20970
No. unique data, restraints, parameters	1562, 0, 125
Final $R1^a$ [$F_o > 4\sigma(F_o)$; $N = 3006$]	0.037
Final $R1,^a$ $wR2^b$ (all reflections; $N = 3462$)	0.043, 0.1023
Goodness of fit^a	1.075

^{a} $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. ^{c} $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$.

Table 2 Selected bond lengths (pm) and angles (°) for $[Cr(NC-Me)_4][BF_4]_2$ **2a**

Cr–N(1)	206.9(2)	N(1)–C(1)	112.1(3)
Cr–N(2)	206.3(2)	N(2)–C(2)	112.6(3)
Cr–F(1)	240.7(2)	C(1)–C(3)	144.7(4)
N(1)–Cr–N(2)	88.85(7)	Cr–N(1)–C(1)	173.2(2)
N(1)–Cr–N(1a)	180.00	Cr–N(2)–C(2)	175.9(2)
N(1)–Cr–N(2a)	91.15(7)	N(1)–C(1)–C(3)	179.2(3)
N(2)–C(2)–C(4)	179.4(2)		

case of **2a**. The low conductivity value measured for a 10^{-3} mol dm⁻³ solution in $MeNO_2$, which is more typical for a 1:1 electrolyte, suggests a comparatively strong association of the chromium(II) cation and the BF_4 anions even in solution.

Taking these data into account complex **2a** may be considered as a square-planar homoleptic dication $[Cr(NCMe)_4]^{2+}$ perturbed by axial interactions with the BF_4^- anions, in close parallel with the situation found for $[Cr(py)_4][(PF_6)_2]$.[13b] Perturbations to the square-planar geometry of chromium(II) complexes are frequent and several types have been described.[15a-c] Interconversions between them can also be very easy as reported for the red (monomeric, square planar)
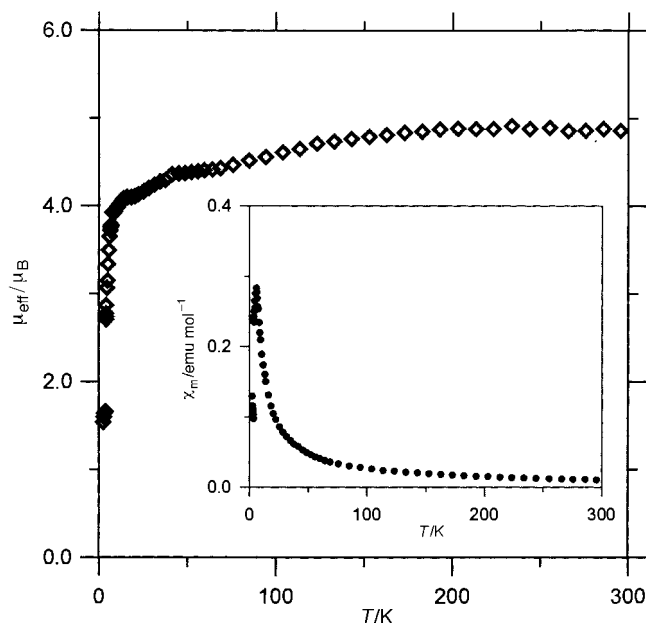
Fig. 2 Temperature dependence of the effective magnetic moment and of the static paramagnetic susceptibility (inset) of [Cr(NCMe)$_4$][BF$_4$]$_2$ **2a** measured at 2T

Scheme 1

and blue (dimeric, five-co-ordinated) forms of [NBu$_4$]$_2$[Cr-(NCS)$_4$],[15d] but other monomeric square-planar chromium(II) complexes have been structurally characterized, *e.g.* [CrBr$_2$-(OH$_2$)$_2$]·2[Hpy]Br,[15e] [Cr(NPh$_2$)$_2$(py)$_2$]·0.5py.[15f] Given its preparation and crystallization in acetonitrile it is noteworthy that not six but only four nitrile ligands surround the Cr. In the electron-richer dications *trans*-[Cr(NCR)$_2$(dmpe)$_2$]$^{2+}$ the co-ordination sphere is octahedral and even in the case of the dimeric complexes [M$_2$(NCMe)$_{10}$]$^{2+}$ (M = Mo,[3d] Rh,[16a] Re[16b] or Tc[16c]) only surrounded by acetonitrile ligands, two axial ligands can be found which are, however, more weakly bonded to the transition-metal M$_2^{4+}$ core than the equatorial ligands. Indeed, complexes of this type without axial acetonitriles are unknown to date. However, some bimetallic complexes whose acetonitrile ligands have been partially substituted by carboxylic acids or diphosphanes lack one or two axial nitrile ligands.[4b–d] The recently described photodissociation of [Tc$_2$(NCMe)$_{10}$][BF$_4$]$_4$ in acetonitrile produces the monomeric complex [Tc(NC-Me)$_6$][BF$_4$]$_2$ with nearly ideal O_h symmetry.[16d]

Magnetic examinations

The ESR data reported for complexes **2a**–**2c** at 4 K are compatible with chromium(II) d^4 high-spin species as the g_{av} values measured are close to the value reported for [Cr(H$_2$O)$_6$]$^{2+}$.[17a] The magnetization results obtained for **2a** yielded an effective magnetic moment at 300 K of 4.9 μ_B in agreement with the value expected for a high-spin d^4 chromium(II) complex with the orbital contribution completely quenched, and reported for [CrX$_2$(NCMe)$_2$][8b] (X = Cl or Br). The temperature dependence (Fig. 2), however, shows a decrease upon cooling indicative of antiferromagnetic interactions. At 4 K a steeper decrease occurs, noticeable both in the μ_{eff} and χ_m *vs. T* curves (inset of Fig. 2), which cannot merely be attributed to the deviation from linearity of the magnetization dependence on the magnetic field accounted by the value of the Brillouin function for that temperature and magnetic field.[17b] It may be the signature of a magnetic transition, either a Néel transition or a high spin–low spin transition ($S = 2$ to $S = 1$). The minimum temperature attained in the ESR experiments (4.5 K) and the lack of single-crystal magnetization measurements do not allow an assignment at this moment. Further magnetic measurements will clarify this point. At present we may only speculate that it is not
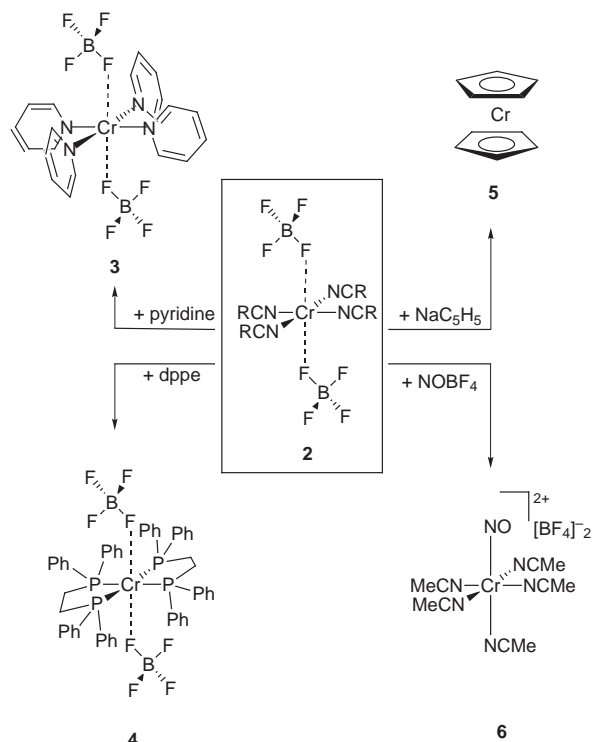
easy to conceive from the crystalline structure how the exchange mechanism can occur, differently from the compounds [CrX$_2$(NCMe)$_2$] where the bridging halide atoms can provide for the magnetic exchange.[8b] On the other hand, spin crossovers occur in several distorted octahedral d^4 complexes in which the amount of distortion can vary with temperature.[17b]

The IR and Raman spectra of complex **2a** were completely assigned. The presence of a center of symmetry is clearly seen from the alternation of the IR and Raman bands below 500 cm^{-1} (metal–ligand motions). Owing to the weak interactions between the CN stretching modes, we were able to detect two IR and Raman pairs of bands rather close to each other which reflect exactly the C_{2h} symmetry. It is also not possible to assign the BF$_4^-$ anions as tetrahedral. The strong splittings of the triply degenerate BF stretching band at 1050 cm^{-1} and the appearance of a symmetric BF$_4$ stretching mode as an IR band at 767 cm^{-1} suggest a lowering of the symmetry. This is consistent with the structural results, showing co-ordination of the BF$_4$ ions to the Cr *via* one fluorine atom. The experimental data and a short discussion have been deposited (SUP 57356).

Reactivity

The lability associated with the nitrile ligands suggests that the highly reducing complexes **2a**–**2c** are a useful and readily available synthetic entry into chromium chemistry. Stirring **2a** in benzonitrile for *ca.* 15 min leads to a complete replacement of the acetonitrile by benzonitrile ligands. Compound **2b** is, in contrast to **2a**, **2c**, not only soluble in other nitriles but also in methylene chloride, chloroform, thf and several other organic solvents. This property renders **2b** a potentially useful starting material for substitution reactions which are no longer hampered by excess of nitrile ligand, as solvent. Treatment of **2b** with an excess of pyridine or dppe as well as with stoichiometric amounts of NaC$_5$H$_5$ or NOBF$_4$ led to the high yield (>90%) formation of, respectively, [Cr(py)$_4$][BF$_4$]$_2$ **3**, [Cr(dppe)$_2$][BF$_4$]$_2$ **4**, [Cr(C$_5$H$_5$)$_2$] **5**[18] and [Cr(NO)(NCMe)$_5$][BF$_4$]$_2$ **6** (Scheme 1).[10] The purification of **6** is sometimes troubled by the presence of some impurities formed in the reaction, but can be achieved by repeated recrystallization. It is readily identified by the characteristic ν(NO) stretching vibration at 1786 cm^{-1} which appears

at 1796 cm^{-1} for [Cr(NO)(NCMe)$_5$][PF$_6$]$_2$.[10] The already mentioned PF$_6^-$ analogue of **3** has been isolated in small yield.[13b] Although samples of a compound analysing correctly for [Cr(py)$_6$][PF$_6$]$_2$ were reported by the same authors,[13b] in our case the analysis was always consistent with the proposed stoichiometry, *i.e.* [Cr(py)$_4$][BF$_4$]$_2$. The IR spectra of **3** and **4** indicate co-ordination of the BF$_4^-$ anions as can be concluded from the triply degenerate BF$_4$ vibrations at *ca.* 1060 cm^{-1}. The symmetric BF$_4$ stretching mode at *ca.* 760 cm^{-1} (768 cm^{-1} for **3**), however, is very close to the dppe vibrations in this region and therefore was not clearly observed for complex **4**. In the case of **4** elemental analysis also consistently rules out the co-ordination of two acetonitrile molecules at the apical positions as was found in the structure of [Cr(dmpe)$_2$(NCMe)$_2$][O$_3$SCF$_3$]$_2$.[13a] This may be surprising in view of the fact that dmpe is a better donor than dppe and, therefore, the latter should favour the co-ordination of two more NCMe ligands when compared to the former. Our only explanation for the absence of these ligands in **4** lies in the empirical observation that the BF$_4^-$ and PF$_6^-$ anions seem to have a preferential tendency to co-ordinate to Cr^{II} relative to the triflate or BPh$_4^-$ anions present as counter ions of [Cr(dmpe)$_2$(NCMe)$_2$]$^{2+}$ and related cations.[13a]

In the case of complex **6**, which was prepared in acetonitrile, one of the five acetonitriles present occupies an apical position. The non-co-ordination of the BF$_4$ is seen from the IR spectrum which only shows one very strong BF$_4^-$ vibration at 1061 cm^{-1} and no band of significant size around 760 cm^{-1}.

These results demonstrate the usefulness of complex **2a** and especially its more soluble analogue **2b** in a variety of synthetic reactions.

Conclusion

We have presented in this paper a structurally characterized example of a chromium(II) complex cation surrounded by nitrile ligands in a square-planar manner. The BF$_4$ counter ions are located at the apical positions of an octahedron, elongated due to Jahn–Teller distortion of the d^4 system. The paramagnetic complexes **2a**–**2c** are easy to prepare but very sensitive to air and moisture. However, this sensitivity foresees varied applications both in synthesis and catalysis. Especially the benzonitrile-substituted complex **2b**, which is not only soluble in nitriles but in a broad variety of other solvents, is a useful starting material for the synthesis of several chromium(II) derivatives.

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