Magnetic Susceptibility and EPR Spectra of μ-Cyano-bis[pentaamminechromium(III)] Perchlorate

Jørgen Glerup* and Høgni Weihe

Department of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark

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The μ-cyano-bis[pentaamminechromium(III)] perchlorate and the analogous cobalt(III) complex have been prepared by a simple synthetic route. The complex behaves as a typical antiferromagnetic coupled chromium(III) dimer with a J value of 32.3(1) cm^{-1}. The EPR spectra of the complex diluted in a frozen glass or diluted with the analogous cobalt(III) complex have been recorded down to 3.8 K. The spectra from the quintet state and from the septet state have been identified by the temperature variation of their intensities. Both spectra have been computer simulated, using the mono-nuclear zero field splitting parameters $D_a + D_b = 0.070(2)$ cm^{-1} and the dinuclear exchange parameter $D_e = -0.0264(1)$ cm^{-1}.

In a search for bridging ligands other than hydroxo and oxo in chromium(III) complexes, we have made some new μ-cyano complexes. Bridged μ-cyano complexes of chromium(III) or cobalt(III) are generally prepared[1-3] by thermal dehydration of neutral salts of an aqua complex in which the anions are typically $[Cr(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ and $[Ni(CN)_4]^{2-}$. We report here the preparation of the three complexes $[(NH_3)_5M\ CN\ M'(NH_3)_5](ClO_4)_5 \cdot 4H_2O$, where the two metal atoms can be Cr and/or Co. The preparations were performed in sulfolane at room temperature or at slightly elevated temperatures by reaction (I),

$$[Cr(NH_3)_5(O_3SCF_3)]^{2+} + [Cr(NH_3)_5CN]^{2+}$$

$$\rightarrow [(NH_3)_5CrCNCr(NH_3)_5]^{5+} + CF_3SO_3^- \qquad (I)$$
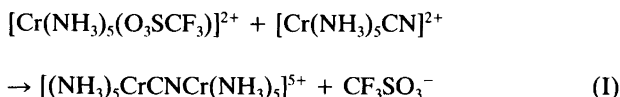
which utilizes the ability of the ligand trifluormethansulfonate to act as a good leaving group. The preparation of μ-cyano-bis[pentaamminecobalt(III)] perchlorate performed in a similar way has recently been reported.[4]

The aim of this investigation was to elucidate the magnetic interactions of the μ-cyano-bridged chromium(III) complex from magnetic susceptibility measurement and the EPR spectra. With the aim of determining the zero field splittings of the two different chromium atoms we attempted to prepare the μ-cyano(N,C)-[pentaamminechromium(III)pentaamminecobalt(III)] perchlorate[†] and the

μ-cyano(C,N)-[pentaamminechromium(III)pentaamminecobalt(III)] perchlorate; however, for reasons not understood by us, we were unable to prepare the last-mentioned complex by the above reaction.

Results and discussion

The magnetic susceptibility. The temperature dependence of the magnetic susceptibility of $[(NH_3)_5CrCNCr(NH_3)_5](ClO_4)_5 \cdot 4H_2O$ was measured in the temperature range 4–300 K as shown in Fig. 1. The susceptibility shows a maximum at approximately 70 K, and the effective magnetic
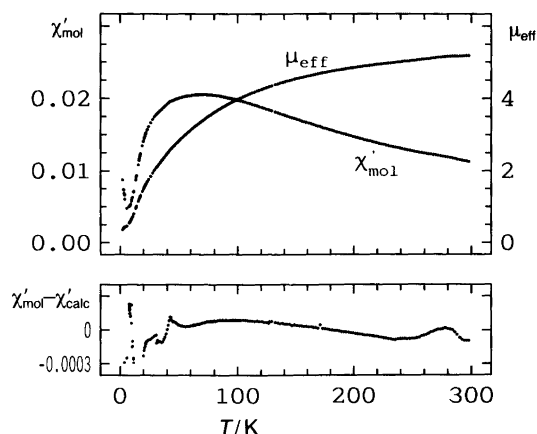

Fig. 1. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment as a function of temperature of $[(NH_3)_5CrCNCr(NH_3)_5](ClO_4)_5 \cdot 4H_2O$. The lower graph gives the difference between the measured and calculated susceptibilities.

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* To whom correspondence should be addressed.

[†] We have extended IUPAC nomenclature[5] by implying that it is the coordinating atoms in parenthesis which are directly bound to the metal atoms in the order given.

moment declines from 5.2 μ_B at room temperature to almost zero at 4 K. This is the expected behaviour characteristic for an antiferromagnetically coupled dimeric chromium(III) complex.

The temperature dependence of the magnetic susceptibility $\chi'_{mol,exp}$ was approximated by eqn. (1) by minimization of expression (2) within the framework of nonlinear regres-

$$\chi'_{mol,exp} \approx \chi'_{mol,calc} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H} \exp{(-E_i/kT)}}{\sum_i \exp{(-E_i/kT)}} + K + C/T \quad (1)$$

$$\sum_T \frac{[\chi'_{mol,exp}(T) - \chi'_{mol,calc}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial\chi}{\partial T}\right)^2 \sigma^2(T)} \quad (2)$$

sion analysis. $\sigma(\chi')$ and $\sigma(T)$ are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. In eqn. (1) C/T accounts for paramagnetic impurities, while K accounts for temperature-independent paramagnetism and minor deviations in the correction for diamagnetism. The energies E_i of the 16 components of the ground-state manifold were obtained by means of the isotropic spin Hamilton operator (3), where

$$\hat{H} = g\mu_B \hat{S}_a \cdot \hat{H} + g\mu_B \hat{S}_b \cdot \hat{H} + J\hat{S}_a \cdot \hat{S}_b \quad (3)$$

we have assumed that the g values for the two chromium atoms are identical. This is an approximation which is only justified because the g values of chromium(III) complexes generally are $g = 1.98(2)$.

The following parameters were obtained: $g = 2.00(1)$ and $J = 32.3(1)$ cm^{-1}. This J value is relative high considering that the π-interaction in the μ-cyano complex has to extend through three bonds compared to two bonds in the μ-hydroxochromium(III) complexes[6-8] and to two bonds in the di-μ-hydroxochromium(III) complexes,[9] where the J values are in the range 21–35 cm^{-1} and in the range 0–43 cm^{-1}, respectively.

In μ-oxo-bis[pentaamminechromium(III)] perchlorate the energy of the septet–singlet separation was expressed as eqn. (4),[10] where $E_{ct} \approx 36000$ cm^{-1} is the energy

$$E_{septet} - E_{singlet} = \frac{\left(\frac{4}{\sqrt{3}}e_{\pi O}\right)^2}{E_{ct}} = 2700 \text{ cm}^{-1} \quad (4)$$

of the observed charge-transfer state and $e_{\pi O} \approx 4300$ cm^{-1}. A similar expression for the μ-cyano-bis[pentaamminechromium(III)] perchlorate gives eqn. (5). This formula is

$$E_{septet} - E_{singlet} = \frac{\left(\frac{4}{\sqrt{3}}(e_{\pi C}e_{\pi N})^{1/2}\right)^2}{E_{ct}}\langle p_C | p_N \rangle^2 = 194 \text{ cm}^{-1} \quad (5)$$

an extension of the expression given in Ref. 11 and accounts for the fact that the two chromium atoms are coordinated to a carbon atom and a nitogen atom, respectively. Furthermore, the matrix element has been expanded over the orbitals of the intervening atoms, which gives rise to the overlap integral between the p-orbitals of the two ligating atoms.

The charge-transfer state has not been observed, but if it is assumed to have an energy of 50000 cm^{-1} the following value for the square root of the e_π parameters times the overlap integral is obtained: $(e_{\pi C}e_{\pi N})^{1/2}\langle p_C | p_N \rangle \approx$ 1270 cm^{-1}. The values for the e_π parameters are not known, but compared with the μ-oxo complex these parameters are smaller and are multiplied with the overlap integral; also the energy of the charge transfer state is higher. These effects together explain the much smaller antiferromagnetic interaction in this complex.

EPR spectra. The X-band EPR spectra of the μ-cyano-chromium(III) dimer were measured at temperatures down to 3.8 K with a frozen glass of the complex dissolved in N-methylformamide as well as with a crystal powder of the complex diluted in the analogous cobalt(III) dimer. The main features of the two sets of spectra are the same. The upper curve in Fig. 2 shows the powder spectrum at 80 K. The intensity versus temperature plot was interpreted in terms of expression (6), which gave $E = 102(10)$ cm^{-1}. This

$$I \propto \frac{1}{T}\frac{\exp{(-E/kT)}}{\sum_i \exp{(-E_i/kT)}} \quad (6)$$

energy corresponds to the quintet state and gives $J = 34(3)$ cm^{-1}, in excellent agreement with the susceptibility data.

The lower curve in Fig. 2 shows the powder spectrum of the μ-cyano-chromium(III) complex diluted in the analagous cobalt(III) complex recorded at 295 K. The plot of intensity versus temperature for the broad line centred around 3400 G was analyzed as before and gave $E = 180(35)$ cm^{-1}. This energy corresponds to the septet state and gives $J = 30(6)$ cm^{-1}, in agreement with the susceptibility data. At lower temperatures the septet spectrum disappeared at approximately 35 K and the quintet spectrum was very weak at 10 K. Below 80 K a weak line at 1650 G was observed. By lowering the temperature the intensity of this line increased relative to the quintet intensities, which might possibly be interpreted as due to part of the triplet spectrum.

The frozen glass spectrum of the μ-cyano dimer measured below 200 K shows no sign of the septet spectrum, in contrast to the powder spectrum. This fact might be ex-
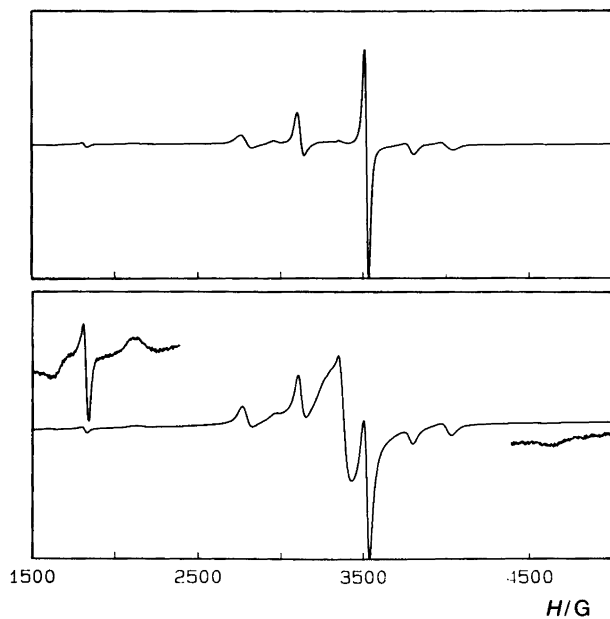
Fig. 2. The powder EPR spectrum of a 1 % of solution of [(NH₃)₅CrCNCr(NH₃)₅](ClO₄)₅·4H₂O diluted in the analogous cobalt(III) complex recorded at 9.37 GHz. The upper curve is measured at 80 K and the lower at 295 K.

plained by different structures in the two media, whereby E_c or the mononuclear z.f.s. parameters (zero field splitting) may be slightly changed. From the crystal structure of [(NH₃)₅CoNCCo(CN)₅] we have the two interesting angles[12] $\angle$NCCo = 172.4° and $\angle$CoNC = 159.8°. If the metal atoms only acted as an acceptor of π-electrons from the cyanide HOMO orbitals a linear structure would be expected, because the hybridization of the carbon and of the nitrogen atoms could then be described as sp-hybridization. The bent structure implies that cobalt(III) donates π-electrons to LUMO orbitals of the cyano bridge, and especially to the carbon end of this, whereby the hybridization on nitrogen will be a linear combination of sp- with some sp^3-hybridization. For the cation μ-cyano-bis[penta-amminechromium(III)]⁵⁺, where the chromium atoms only have half-filled π-orbitals, one would expect that the donation of π-electrons to the LUMO orbitals is less pronounced than in the cobalt(III) complex, i.e. the chromium complex is more linear than the analogous cobalt complex. Dilution by the cobalt complex has enforced a greater bending on the chromium complex. The following interpretation of the EPR spectrum of μ-cyano(N,C)[penta-amminechromium(III)pentaamminecobalt(III)] complex shows that this is also non-linear.

Interpretation of EPR spectra. The spectrum recorded at 80 K in Fig. 2 is a typical quintet spectrum, which can easily be interpreted only when it is realised that the outer two z-components can be observed at ca. 2100 and ca. 4700 G. The quintet and the septet spectrum

were simulated by means of the spin Hamilton operator (7), where $\hat{H}_{ex}$ is given by eqn. (8) and $\hat{H}_a$ by eqn. (9),

$$\hat{H} = \hat{H}_a + \hat{H}_b + \hat{H}_{ex} \tag{7}$$

$$\hat{H}_{ex} = J\vec{S}_a \cdot \vec{S}_b + D_c(2S_{az}S_{bz} - S_{ax}S_{bx} - S_{ay}S_{by}) + E_c(S_{ax}S_{bx} - S_{ay}S_{by}) \tag{8}$$

$$\hat{H}_a = g\mu_B\vec{S}_a \cdot \vec{H} + D_a[S_{az}^2 - 1/3S_a(S_a + 1)] + E_a(S_{ax}^2 - S_{ay}^2) \tag{9}$$

with a similar Hamilton operator for atom b. Again it has been assumed that the g values for the two chromium atoms are identical. Here a refers to the N-bonded chromium and b to the C-bonded chromium.

The quintet and septet spectra were simulated with the following parameter values: $J = 32.3\,\text{cm}^{-1}$, $g = 1.985$, $D_c = -0.0264(1)\,\text{cm}^{-1}$ and with $D_a + D_b = 0.070(2)\,\text{cm}^{-1}$. We have here assumed D_c to be negative, because this parameter can be written as a sum of a dipolar and a pseudo-dipolar term,[13] and with an assumed bond distance of 5.0(1) Å the dipolar term is calculated to be $-0.0140(15)$ cm^{-1}. There is another solution to the simulation of the quintet and the septet spectra, where instead of 0.070(2) cm^{-1} $D_a + D_b$ is 0.168(2) cm^{-1}. This solution has been rejected not on the basis of the simulation but on the basis of a discussion of the z.f.s. of the two chromium atoms (*vide infra*).
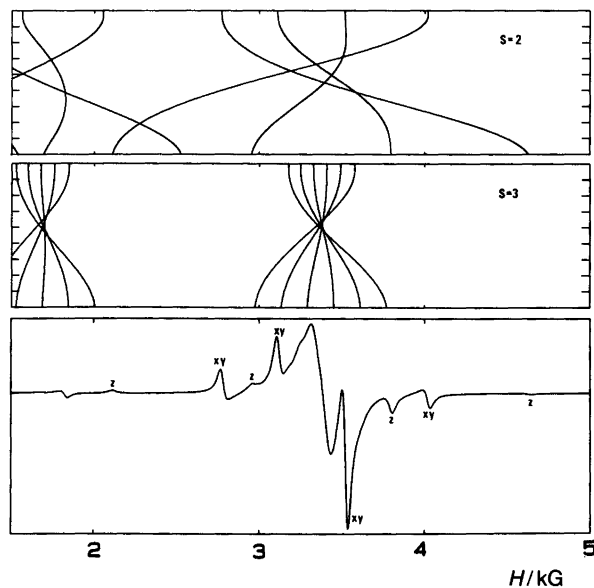

Fig. 3. The simulated EPR spectrum calculated at 295 K of [(NH₃)₅CrCNCr(NH₃)₅](ClO₄)₅·4H₂O. The spectrum is constructed by addition of the simulated quintet and septet spectra properly weighted by the Boltzmann factor at 295 K. The upper graphs show the angular dependence of the resonance condition for the quintet and the septet, respectively, where the ordinate is the angle between the z-axis of the molecule and the magnetic field. The lower graph shows the simulated spectrum, where the symbols x, y and z gives the orientation of the magnetic field relative to the molecular coordinate system for the quintet spectrum.

Fig. 3 gives the simulated spectra of the quintet and the septet added together and properly weighted with the Boltzmann factor at 295 K. It has been necessary to assume the linewidth for the quintet to be 60 G and for the septet to be 120 G. The agreement with the experimental spectrum is excellent. From the angular dependence of the resonance condition in Fig. 3 it is seen that the quintet spectrum is much more extended than the septet spectrum, which can be explained by the fact that the diagonal elements in the septet part of the matrix become accidentally small.

The quintet spectrum is almost independent of the local zerofield splitting parameters D_a and D_b, which means that these parameters can not be determined from the quintet spectrum, and from the septet spectrum one can only determine their sum. Simulation of the triplet spectrum with the parameters given above cannot explain the line at 1650 G observed below 80 K, and we conclude that it is caused by an unknown impurity. It can be stated here that the formulae for the effective spin Hamilton operator given by Harris and Owen[13] is a bad approximation for simulation of, especially, the triplet spectrum (cf. Ref. 14).

We hoped to be able to estimate the individual z.f.s. parameters from the interpretation of the EPR spectra of the μ-cyano(N,C)-[pentaamminechromium(III)penta-amminecobalt(III)] complex and of the μ-cyano(C,N)-[pentaamminechromium(III)pentaamminecobalt(III)] complex. From computer simulation of the first complex we can conclude $|D_a| \approx 0.070$ cm^{-1} and $|E_a| \leq 0.003$ cm^{-1}, but because we could not prepare the second complex we must estimate D_b in another way.

The EPR spectrum of $[Cr(NH_3)_5CN]^{2+}$ consists of a broad band centred around $g = 2$ with no observed splittings, which gives $D \approx 0.00(2)$ cm^{-1}. On the other hand it is possible to estimate the sign and order of magnitude of the z.f.s. from the calculated splitting of the $^4T_{2g}$ state of the cation $[Cr(NH_3)_5CN]^{2+}$. With the values $\Delta_N = 21.600$ cm^{-1} (Ref. 15) and $\Delta_{CN}=26.600$ cm^{-1} (Ref. 16) one obtains eqn. (10),

$$D_b = \frac{8}{9} \frac{\zeta^2(^4B_2 - {}^4E)}{\Delta_{av}^2} \approx -0.15 \text{ cm}^{-1} \tag{10}$$

where a value of $\zeta = 273$ cm^{-1} has been used[17] for the spin–orbit coupling constant. A discussion of this formula in relation to diagonalization of the energy matrix for the d^3 configuration is given by Pedersen and Toftlund.[18]

We can conclude that $D_a + D_b = 0.070(2)$ cm^{-1} is in agreement with the sum of the measured D values for the two ions $[Cr(NH_3)_5CN]^{2+}$ and $[(NH_3)_5CrNCCo(NH_3)_5]^{5+}$, whereas $D_a + D_b = 0.168(2)$ cm^{-1} and $D_a \approx 0.07$ cm^{-1} gives an unrealistic value for the parameter $D_b \approx 0.097$ cm^{-1}.

UV–VIS spectra. The spectrum of the μ-cyano-bis[penta-amminechromium(III)] complex is shown in Fig. 4. The maximum at 457 nm shows that the energy of the first spin-allowed transition is placed between the maxima for the two ions $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5CN]^{2+}$, as ex-
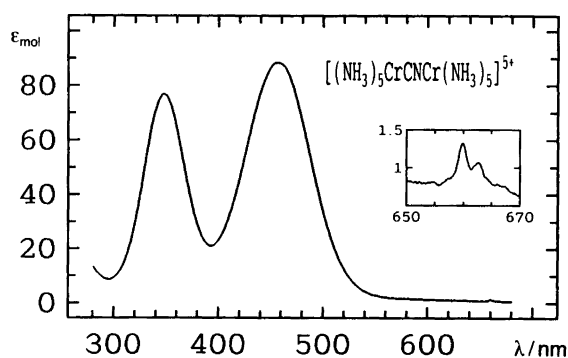

Fig. 4. The absorption spectrum of [(NH₃)₅CrCNCr(NH₃)₅]-(ClO₄)₅·4H₂O dissolved in water.

pected. Riccieri *et al.*[19] state that the intensity of the spin-forbidden transitions of the cation $[Cr(NH_3)_5CN]^{2+}$ are so weak that they can barely be observed in absorption spectroscopy, but are moderately intense in luminescence spectroscopy. The intensity of the μ-cyano complex in this region as seen in Fig. 4 is further proof of the exchange interaction between the two chromium atoms, which gives a considerable intensity enhancement.[10,20] The spectra of the analogous cobalt(III) complex and of the mixed μ-cyano(N,C)-[pentaamminechromium(III)pentaammine-cobalt(III)] complex are given in Fig. 5.

Experimental

Magnetic measurement. The Faraday balance for the susceptibility measurements has been described elsewhere.[11] The measurements were performed at a field strength of 13 kG.

EPR spectra. The EPR spectra were recorded with a Bruker ESP 300 spectrometer equipped with an Oxford ESR-900 continous flow cryostat. The spectra were
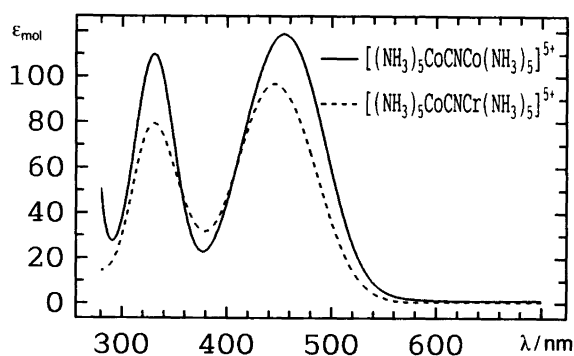

Fig. 5. The absorption spectra of [(NH₃)₅CoCNCo(NH₃)₅]-(ClO₄)₄·4H₂O (——) and of [(NH₃)₅CrNCCo(NH₃)₅](ClO₄)₅·4H₂O (----) dissolved in water.

recorded at 9.37 GHz, 20 mW microwave power and with a modulation frequency 100 kHz and a modulation amplitude of 5 G.

Computer simulations. The simulation of the EPR spectrum was performed by generating an energy matrix of dimension 16 for each orientation of the molecule relative to the magnetic field. The resonance condition for each transition was then found by successive diagonalizations and iterations and the relative intensity was calculated from the eigenvectors. Summation of all the transitions over the whole space, where each transition is represented by a differentiated Lorentzian curve, gives the simulated spectrum. A more detailed description of the numerical method will be given elsewhere.

VIS spectra. The UV–VIS spectra were recorded in the interval 700–250 nm with a Perkin-Elmer Lambda 17 spectrophotometer.

Materials. Sulfolane was dried at $30\,^{\circ}C$ over 3 Å molecular sieves for several days before use. $[Co(NH_3)_5CN](ClO_4)_2$ was prepared by storing the hemihydrate[21] in a vacuum desiccator over P_2O_5 for 5 days. The compounds $[Cr(NH_3)_5CN](ClO_4)_2$,[19] $[Co(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ and $[Cr(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$[22] were prepared according to published methods. All other chemicals used were of analytical grade and were used without further purification.

Preparations

1. μ-Cyano-bis[pentaamminechromium(III)] perchlorate tetrahydrate, $[(NH_3)_5CrCNCr(NH_3)_5](ClO_4)_5 \cdot 4H_2O$. 16.5 g (45.6 mmol) of $[Cr(NH_3)_5CN](ClO_4)_2$ were dissolved in sulfolane (125 ml) preheated to $60\,^{\circ}C$ and 26.6 g (45.6 mmol) of $[Cr(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ were added. The flask was fitted with a tight stopper and stirred magnetically at room temperature. After 4 h a 'porridge' consistency was obtained, and ethanol (300 ml) was added. The resulting precipitate was filtered off and washed with ethanol. The crude product was dissolved in perchloric acid (0.001 M) preheated to $40\,^{\circ}C$, and precipitated by slow addition of 50 ml saturated $NaClO_4$. The yellow crystals were isolated and washed with ethanol. Yield 26.5 g (73 %). Found: Cr 11.92; C 1.32; N 17.37; Cl 21.82; Calc. Cr 11.96; C 1.38; N 17.71; Cl 20.38.

2. μ-Cyano(N,C)-[pentaamminechromium(III)pentaamminecobalt(III)] perchlorate tetrahydrate, $[(NH_3)_5CrNCCo(NH_3)_5](ClO_4)_5 \cdot 4H_2O$. This compound was prepared in a similar way to preparation 1. 5.0 g (13 mmol) $[Co(NH_3)_5CN](ClO_4)_2$ and 8.0 g (14 mmol) $[Cr(NH_3)_5(O_3SCF_3)]$-$(O_3SCF_3)_2$ were used. After recrystallisation the yield was 9 g (79 %). Found: Co 6.67; Cr 5.96; C 1.31; N 17.12; Calc. Co 6.72; Cr 5.93; C 1.37; N 17.58.

3. μ-Cyano-bis[pentaamminecobalt(III)] perchlorate tetrahydrate, $[(NH_3)_5CoCNCo(NH_3)_5](ClO_4)_5 \cdot 4H_2O$. This compound was prepared in a similar way to preparation 1. 10.0 g (27 mmol) $[Co(NH_3)_5CN](ClO_4)_2$ and 16.0 g (27 mmol) of $[Co(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ were used. After recrystallisation the yield was 16.6 g (70 %). Found: Co 13.15; C 1.25; N 17.12; Calc. Co 13.34; C 1.36; N 17.44.

4. Attempt to prepare μ-cyano(C,N)-[pentaamminechromium(III)pentaamminecobalt(III)] perchlorate. The attempt was performed in a similar way to preparation 1. 3.2 g (8.7 mmol) $[Cr(NH_3)_5CN](ClO_4)_2$ and 5.1 (9.9 mmol) $[Co(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ were used. Several recrystallisations gave a greyish-yellow powder which could not be analysed properly.

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