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Article

Synthesis, Crystal Structure, and Magnetic Properties of μ-Hydroxo-bis[pentakis(acetonitrile)chromium(III)] Tetrafluoroborate: An Acetonitrile Analogue to “Acid Rhodo”

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The reaction of $[Cr(NCCH_3)_6]^{2+}$ with dioxygen in acetonitrile (MeCN) solution acidified with HBF_4 gave red crystals of the binuclear complex $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5](BF_4)_5$ (**1**). From the X-ray crystal structure of **1**, the Cr–O–Cr angle was found to be 147.5(2)°. Magnetic susceptibility measurements of **1** showed an antiferromagnetic coupling between the two chromium(III) centers with a triplet energy $J = 35.9(1)$ cm^{-1}. On redissolution of **1** in MeCN, the hydroxo bridge was deprotonated, and a green solution of the complex $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ formed. The electronic absorption spectrum of this solution is very similar to the spectrum of the classical complex $[(H_3N)_5CrOCr(NH_3)_5]^{4+}$ with intense bands in the UV and near-UV region. From the temperature dependence of the absorption spectrum near 12900 cm^{-1}, the triplet energy J was found to be 1067(19) cm^{-1}. The acidity of the hydroxo bridge in **1** is very high with an acid dissociation constant $K_a \gg 1$ M.

Introduction

The substitution of the acetonitrile (MeCN) ligands by other ligands, either charged or neutral, occurs fast in the homoleptic MeCN complexes of the divalent metals in the first transition series,[1] and MeCN complexes have accordingly found extensive use as synthetic precursors for novel coordination compounds, especially if nonaqueous conditions are required.

The present contribution deals with the chromium(II) complex $[Cr(NCCH_3)_6]^{2+}$. This complex has been isolated in the solid state as a tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (tfpb$^-$) salt by Miller.[2] In another report,[3] Kühn used tetrafluoroborate as an anion and isolated the compound $[Cr(NCCH_3)_4(FBF_3)_2]$ with the two BF_4^- anions coordinated *trans*. We discovered that a blue MeCN solution of $[Cr(NCCH_3)_6]^{2+}$ acidified with HBF_4 turned red on exposure to dioxygen at room temperature and that red crystals subsequently formed. A crystal structure determination revealed that the oxidation had led to formation of the title compound $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5](BF_4)_5$. The cation in this salt is an MeCN analogue to the classical complex $[(H_3N)_5Cr(OH)Cr(NH_3)_5]Cl_5$ (the so-called “acid rhodo”) first prepared by Jørgensen in 1882.[4] We report in this paper the synthesis, crystal structure, and magnetic, optical, and acid/base properties of the title compound along with spectroscopic studies of its corresponding base, $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$.

Experimental Section

The compounds $[Cr(NCCH_3)_4(FBF_3)_2]$ and $[Cr_2(O_2CCH_3)_4]$ were prepared according to literature methods.[3,5] HBF_4 in diethyl ether (54%, $d = 1.18$) was purchased from Merck. MeCN was dried over molecular sieves (resulting in a water content of 10−15 ppm according to a Karl Fischer titration) and purged with dinitrogen prior to use. The reaction flasks were flame-dried prior to use.

Synthesis of $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5](BF_4)_5$ (1). Method 1. To a suspension of $[Cr_2(O_2CCH_3)_4]$ (0.45 g, 1.3 mmol) in MeCN (4 mL) was added HBF_4 (1.0 mL, 7.3 mmol) under stirring and under a dinitrogen atmosphere in a Schlenk tube. The stirring was continued until all $[Cr_2(O_2CCH_3)_4]$ was dissolved. The resulting blue solution was then without stirring exposed to dioxygen (no stirring or bubbling). During 2−3 h, the color of the solution changed to red, and red crystals suitable for X-ray crystallography

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formed. The mother liquor was decanted off, and the crystals were washed with MeCN acidified with a few drops of HBF_4 followed by diethyl ether. The crystals of **1** were dried under a dinitrogen flow. The yield was 0.50 g (40%). Anal. Calcd for $C_{20}H_{31}B_5Cr_2F_{20}N_{10}O$: C, 24.88; H, 3.24; Cr, 10.77; N, 14.51. Found: C, 24.50; H, 3.49; Cr, 10.49; N, 14.20%. The product is very moisture-sensitive and should be kept at −20 °C.

Method 2. Under a dinitrogen atmosphere, $[Cr(NCCH_3)_4(FBF_3)_2]$ (1.0 g, 2.6 mmol) was dissolved in MeCN (5 mL), and HBF_4 (200 μL, 1.4 mmol) was then added. The solution was exposed to dioxygen, and product **1** was isolated as described in the same yields.

X-ray Crystallography. Crystal data for **1**: $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5](BF_4)_5$, formula weight = 965.60, monoclinic, space group $C2/c$ (No. 15), $a = 13.9060(3)$ Å, $b = 15.4350(6)$ Å, $c = 19.0080(17)$ Å, $\beta = 97.201(4)°$, $V = 4047.7(4)$ Å^3, $Z = 4$, $D_c = 1.585$ g cm^{-3}, μ(Mo Kα) = 0.662 mm^{-1}, 63447 measured reflections, 5912 independent reflections, $R_{int} = 0.0725$, $R(F^2 > 2\sigma(F^2)) = 0.0712$, $R_w(F^2) = 0.2042$. Single-crystal X-ray data collection was performed at 122(1) K with Mo Kα radiation ($\lambda = 0.71073$ Å) with a Nonius Kappa-CCD area-detector diffractometer employing ω and Φ scan modes to $\theta_{max} = 30.0°$. The cell parameters were determined from 118 reflections with $4.0° < \theta < 21.6°$. Data collection was performed using COLLECT.[6] Unit cell refinement and data reduction were performed using the programs DIRAX[7] and EvalCCD.[8] Absorption correction was not applied. The structure was determined by direct methods using the SHELXS97 program,[9] and the refinement was carried out by full-matrix least-squares refinement against F^2 using SHELXL97.[9] All non-hydrogen atoms were refined anisotropically, and all methyl hydrogen atoms were included in idealized positions with fixed C−H distances and isotropic thermal parameters constrained to $1.5U_{eq}$ of the parent atom. The hydroxo hydrogen atom was identified as a peak in the difference electron density maps, and its positional parameters were refined with a fixed U_{eq} of 0.03 Å^2. In the space group $C2/c$, the cation lies on a crystallographic 2-fold axis, and the bridging oxygen lies off the axis and is thus disordered with half occupancy at each site. In this description, the anisotropic displacement parameters of the hydroxo oxygen are comparable to those of the surrounding non-hydrogen atoms and do not suggest any further disorder. Two of the BF_4^- anions display disorder, which is not unusual in BF_4^- groups. In one, the B atom lies on a special position, and the occupancy of the two conformations of the anion is 0.5. In the other disordered anion, the occupancies of the two conformations are 0.65(2) and 0.35(2). Attempts to refine the structure in the subgroups Cc, $C2$ and $P\bar{1}$ resulted in disorder of the bridging oxygen and strong correlation between the parameters related by noncrystallographic symmetry.

Other Physical Measurements. Absorption spectra were recorded on a Varian Cary 5E UV−vis−NIR spectrophotometer. Low temperature absorption spectra were performed applying a DN-type liquid nitrogen cryostat from Oxford Instruments to the spectrophotometer. The temperature was set manually via an ITC502 T-controller. The thermal expansion coefficient α_V for MeCN was found in the literature[10] to be 1.389×10^{-3} K^{-1}. Kinetic runs were performed on a Perkin-Elmer Lambda 40 UV−vis spectrophotometer equipped with a thermostated cell holder. Elemental analyses of C, H, and N were done at the Microanalytical Laboratory at our Department of Chemistry. The magnetic susceptibility was measured by the Faraday method in the temperature range 4.6−300 K. A description of the instrument is given elsewhere.[11]

Results and Discussion

Synthesis. In the synthesis of **1**, strictly anhydrous conditions were necessary in order to obtain reasonable yields. Compound **1** was prepared from $[Cr(NCCH_3)_6]^{2+}$ by the reaction with dioxygen in MeCN solution in the presence of acid according to eq 1:

$$4[Cr(NCCH_3)_6]^{2+} + O_2 + 2H^+ \rightarrow 2[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5]^{5+} + 4CH_3CN \quad (1)$$

An acidic MeCN solution of the complex $[Cr(NCCH_3)_6]^{2+}$ can be prepared either by dissolving $[Cr_2(O_2CCH_3)_4]$ with excess of HBF_4 in MeCN (method 1) or by dissolving the compound $[Cr(NCCH_3)_4(FBF_3)_2]$ in MeCN followed by addition of HBF_4 (method 2).

Attempts to redissolve solid **1** in MeCN resulted surprisingly in an immediate formation of a green solution. Addition of HBF_4 to the green solution caused an immediate color change to red and a reprecipitation of **1** at sufficiently high complex concentration. These reactions are therefore protolytic, and the identity of the green species is accordingly $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$. In support of this, the absorption spectrum of the green solution (Figure 1b) resembles the spectrum[12] of the so-called “basic rhodo”, $[(H_3N)_5CrOCr(NH_3)_5]^{4+}$, first prepared by Jørgensen in 1882.[4] Exposure of a MeCN solution of $[Cr(NCCH_3)_4(FBF_3)_2]$ to dioxygen without previous addition of HBF_4 gave a green solution with the same spectrum as in Figure 1b. Kühn also noted that solutions of $[Cr(NCCH_3)_4(FBF_3)_2]$ turned greenish upon exposure to dioxygen, but the nature of the oxidation product was not commented on.[3] It should also be mentioned here that Miller[2] published an absorption spectrum of a solution made by air oxidation of an MeCN solution of $[Cr(NCCH_3)_6](tfpb)_2$. The spectrum is qualitatively identical to the spectrum in Figure 1b, but the values of ϵ in Miller’s spectrum are a factor of 2 lower probably owing to decomposition of the product. The nature of the oxidation product was not discussed.

Crystal Structure. As shown in Figure 2, the Cr atoms in **1** are octahedrally coordinated to five MeCN ligands and one bridging hydroxo ligand. The Cr−N distances and the Cr−N−C angles fall in the range 1.994(3)−2.011(3) Å and 170.6(3)−178.2(3)°, respectively. These values are normal for this type of compound. The crystal structure of the classical “acid rhodo” complex has most recently been reported by Harris et al.[13] In this structure, there are two

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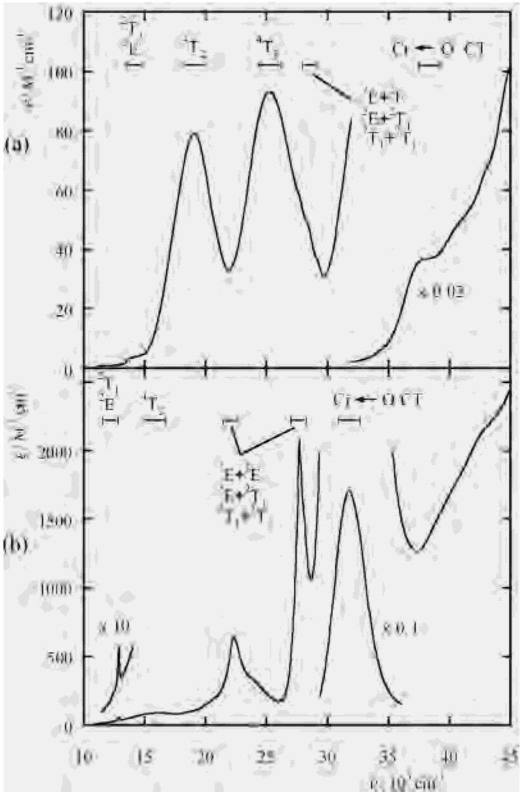

Figure 1. Absorption spectra ($T = 298$ K) with the maxima given as described in parentheses ($\tilde{\nu}_{max}/10^3$ cm^{-1}, ϵ/M^{-1} cm^{-1}) and the assignments in O_h single-ion notation. (a) $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5]^{5+}$ in MeCN acidified with HBF_4, (19.1, 78.9) and (25.3, 93.0). (b) $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ in MeCN, (12.9, 56.5), (16.2, 85.8), (22.3, 640), (26.2, 183), (27.7, 2080), and (31.8, 17000).

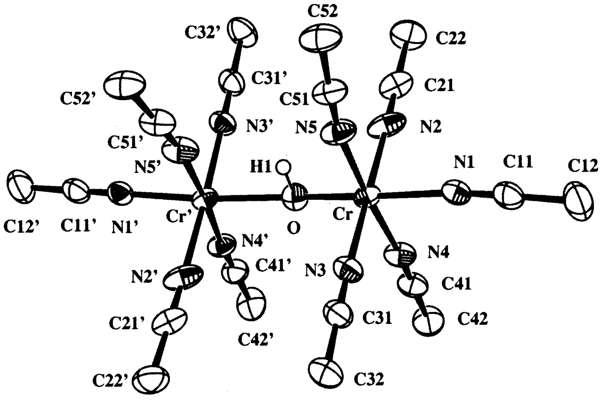

Figure 2. Molecular structure of the $[CH_3CN)_5Cr(OH)Cr(NCCH_3)_5]^{5+}$ cation. The two halves of the molecule are related by a crystallographic 2-fold (C_2) axis. Atoms marked by primes (′) are related to the corresponding unmarked atoms by the C_2 axis. The bridging hydroxo ligand is disordered over two sites with half occupancy each. Only one site is shown here. The thermal ellipsoids are shown at the 50% probability level. For clarity, the methyl hydrogen atoms have been omitted.

independent molecules in the asymmetric unit, and the Cr−N distances fall in the range 2.051−2.096 Å, which is systematically higher than those found in **1**, corresponding to the lack of delocalization of π orbitals in "acid rhodo". In "acid rhodo", the Cr−O bond lengths were found to be slightly asymmetric, with Cr1−O and Cr2−O of 1.985(3) and 1.975(3) Å in one molecule and 1.973(3) and 2.006(3) Å in the other. This asymmetry is even more pronounced in **1**, where the Cr−O and Cr′−O bond lengths are 1.904(5) and 1.998(5) Å, respectively. The asymmetry in **1** can be explained by the formation of an intramolecular hydrogen bond between O−H1···N5. The O−H1 distance is 1.06(6) Å, the O−N5 distance is 2.943(6) Å, and the O−H1···N5 angle is 130(6)°. In "acid rhodo", this type of intramolecular hydrogen bond cannot occur, and instead, the bridging hydroxo groups form intermolecular hydrogen bonds with chloride ions. The intramolecular hydrogen bond in **1** may also explain why the Cr−O−Cr′ angle at 147.5(2)° is smaller than the two angles of 154.88° and 154.38° found in "acid rhodo", and as a consequence, the Cr−Cr′ distance in **1** of 3.7455(9) Å is shorter than the two Cr1−Cr2 distances in "acid rhodo" of 3.8638(14) and 3.8789(15) Å, respectively. Apart from the intramolecular hydrogen bond, all remaining hydrogen bonds in **1** are of the type C−H···F.

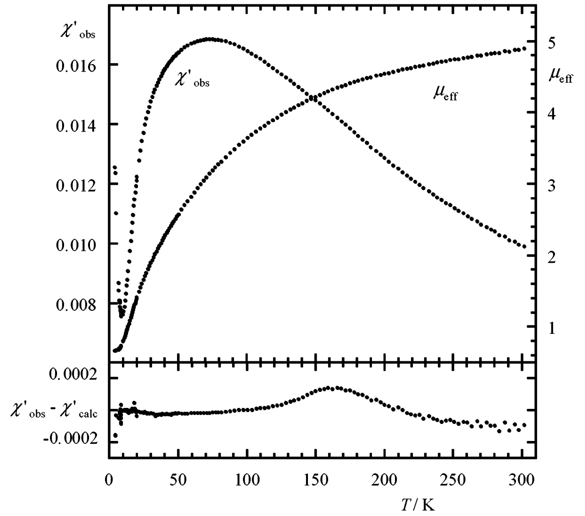

Figure 3. Magnetic susceptibility (χ'_{obs}) in cgs units and the effective magnetic moment (μ_{eff}) of $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5](BF_4)_5$ vs the temperature. The lower graph shows the difference between the observed and calculated values of χ'. The irregularities of the lower graph in the temperature range 200−300 K could be due to loss of coordinated MeCN ligands due to the low pressure in the cell (~1 mbar).

Magnetic Properties. A plot of the magnetic susceptibility of **1** versus temperature is shown in Figure 3. A least-squares fit of eq 2 which is based[14] on the van Vleck Hamiltonian $\mathbf{H} = JS_1S_2$, where the triplet, quintet, and septet energies are J, $3J$, and $6J$, respectively, gave $J = 35.9(1)$ cm^{-1}, $g = 1.966(4)$, TIP $= 89(3) \times 10^{-4}$, and $x_p = 0.0528(1)$.

$$\chi' = (1 - x_p) \times \frac{Ng^2\mu_B^{\ 2}}{kT}\,\frac{2\exp(-J/kT) + 10\exp(-3J/kT) + 28\exp(-6J/kT)}{1 + 3\exp(-J/kT) + 5\exp(-3J/kT) + 7\exp(-6J/kT)} + 2x_p\frac{Ng^2\mu_B^{\ 2}}{3kT}S(S+1) + \mathrm{TIP} \quad (2)$$

Here, x_p is the fraction of Cr(III) present as mononuclear species ($S = {}^3/_2$). Several attempts to prepare samples with a lower content of mononuclear impurities were unsuccessful. Values of J in other singly hydroxo-bridged chromium(III) dimers have been found in the range 20−36 cm^{-1}, and there appears to be some correlation with the value of the Cr−

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O−Cr angle.[14−17] In "acid rhodo", *J* has by susceptibility measurements previously been found by Hodgson[14] and Glerup[15] to be 31.5 and 32.3 cm^{-1}, respectively. This is close to the value for **1**, which is not surprising since the Cr−O−Cr angle differs by only 7°.

Electronic Absorption Spectra. The room temperature absorption spectrum of **1** recorded in MeCN acidified with HBF_4 is shown in Figure 1a. The spectrum is typical for a weakly coupled chromium(III) dimer.[18] The energy of the $^4T_2 \leftarrow {}^4A_2$ (O_h) transition (19100 cm^{-1}) is lower than in "acid rhodo" (20000 cm^{-1})[19] in accordance with the relative position of the MeCN and ammonia ligand in the spectrochemical series.[20] Single excitations are located in the range 14000−15000 cm^{-1}, and double excitations are seen as shoulders in the range 28000−29300 cm^{-1}. The transition at 38000 cm^{-1}, also seen in other hydroxo-bridged chromium(III) dimers,[21] is likely to be a Cr ← O CT.

The spectrum of $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ in MeCN[22] shown in Figure 1b is very similar to the spectrum of "basic rhodo" which has been assigned by Glerup[12] and Güdel.[23] The most notable features are the intense transitions in the near-UV and UV range. A very intense band ($\epsilon > 10^4$ M^{-1} cm^{-1}) in the UV range is typical for complexes containing a linear $Cr^{III}OCr^{III}$ chromophore (in the present case located at 31800 cm^{-1} with $f \approx 0.2$), and it has been proposed[23,24] to be of mainly Cr ← O CT (LMCT) character probably with some Cr ← Cr CT (MMCT) character. The remaining transitions in the UV and near-UV range are single and double excitations. The single and double excitations in $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ are 1400−2200 cm^{-1} (8−12%) lower in energy than the corresponding excitations in "basic rhodo". The transitions from the $^4A_2$ (O_h) ground state to the ^2E and $^2T_1$ (O_h) states occur within the same electron subconfiguration (t_2^3, O_h), and their energies are (to a first order) equal to $9B + 3C$, where B and C are the Racah interelectronic repulsion parameters.[25] The lower repulsion in **1** compared to "basic rhodo" is attributed to a delocalization of the electrons. As noted earlier, the MeCN ligands possess π orbitals in contrast to the ammonia ligands. A π overlap between metal t_2 orbitals and empty π^* orbitals on the nitrogen atoms could therefore result in such a delocalization. The energy of the LMCT transition is 4100 cm^{-1} (12%) lower than in "basic rhodo". Part of the explanation could again be the reduction of the interelectronic repulsion on the metal center. Another contribution to this reduction could be attributed to the fact that the one-electron energy of the t_2 orbitals (O_h) is lowered as a result of the π acidity of the MeCN ligands thereby lowering the energy gap between the oxygen p orbitals and the metal $t_2(O_h)$ orbitals.

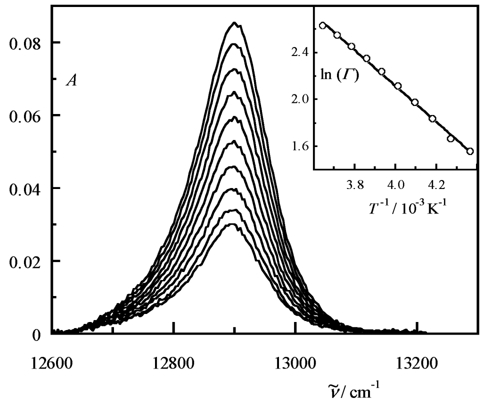

Figure 4. Absorption spectra of $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ in MeCN in the range 12600−13300 cm^{-1} at the temperatures 229.0 (lower), 234.2, 239.2, 244.2, 249.2, 254.2, 259.2, 264.2, 269.2, and 274.3 K (upper). The inset shows a plot of the natural logarithm of the integrated absorption intensity $\Gamma = \int A(\tilde{\nu})\tilde{\nu}^{-1}\, d\tilde{\nu}$ in the range 12600−13200 cm^{-1} vs T^{-1}. The markers (○) represent the experimental data and the line represents a least-squares fit of a straight line to the data yielding a slope of 1535(28) K corresponding to a triplet energy *J* of 1067(19) cm^{-1}.

The band at 12900 cm^{-1} ($f \approx 2 \times 10^{-5}$) is a hot band, originating from transitions from the $S = 1$ state, with an intensity proportional to the Boltzmann factor $\exp(-J/kT)$, where J is the triplet energy.[26,27] A study of the temperature dependence of the integrated absorption intensity, Γ, will accordingly give the value of J in $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$. This is shown in Figure 4 where the spectra recorded in MeCN in the temperature range 229−274 K are shown. At higher temperatures, the rate of the decomposition of the complex was too high.[22] The spectra have been corrected for background, and a second-order polynomial baseline has been subtracted. Furthermore, the absorbances were corrected for the thermal expansion of the solvent. From a plot of ln(Γ) vs T^{-1} (Figure 4, inset), $J = 1067(19)$ cm^{-1} was calculated from the slope of the straight line, obtained from a least-squares fit. In the "basic rhodo", Dubicki, Martin, and Güdel[23,28] found by the same method that $J = 400-500$ cm^{-1}, a value in agreement with a later determination of J by Pedersen[29] from magnetic susceptibility measurements (450 ± 2 cm^{-1}). The much stronger exchange coupling in $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ compared to "basic rhodo" is noteworthy. Weihe, Güdel, and Toftlund[30] have for a chromium(III) dimer found a correlation (eq 3) between J and the LMCT and MMCT transition energies, hereafter called Δ and U, respectively.

$$J = \frac{8}{9}\frac{{V_{p\pi}}^4}{\Delta^2}\left(\frac{1}{U} + \frac{1}{\Delta}\right) \tag{3}$$

Here, $V_{p\pi}$ denotes the hybridization matrix element describing the one-electron interaction between O^{2-} and Cr^{3+}.

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[22] The complex $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ is unstable in MeCN. A first-order decay with a half-life of ∼20 min at room temperature was observed.
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[26] One referee pointed out that transitions from the $S = 2$ state are more intense. Calculations performed as shown in ref 27 show that the oscillator strength of the transitions from the $S = 2$ state is a factor of 3 higher than transitions from the $S = 1$ state. However, for $J > 200$ cm^{-1}, the thermal population of the $S = 2$ state is so low that transitions from this state are not observed.

A lower value of Δ for the LMCT transition will accordingly give a higher value of J, and this is in agreement with the observation that the value of Δ in $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ for the above-mentioned reasons is ~10% lower than the value in "basic rhodo". The value of U is the energy of the MMCT transition $Cr^{4+}, Cr^{2+} \leftarrow Cr^{3+}, Cr^{3+}$ $(t_2{}^2,t_2{}^4 \leftarrow t_2{}^3,t_2{}^3)$, and this can be calculated to $A + 10B + 5C$.[31] Lower values of the Racah interelectronic repulsion parameters will also lead to an increase of J. A 12% reduction of U and Δ will according to eq 3 thus account for a factor of ~1.5 increase of J. Finally, a shorther Cr−O bond length in $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ than in "basic rhodo", which results in a higher value of $V_{p\pi}$, could also contribute to the increased exchange coupling. Efforts to grow crystals suitable for X-ray crystallography of a salt of the complex $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ in order to determine the Cr−O bond length have so far been unsuccessful. It should be mentioned that the shoulder at 24000 cm^{-1} in Figure 1b almost disappears on cooling to 229 K, and it is thus originating from another hot transition. It is, however, not possible to obtain a value of J from these data because the spectrum in this range could not be satisfactory resolved into single Gaussian curves. Noteworthy is that the crystal structure of the analogous molybdenum complex $[(CH_3CN)_5MoOMo(NCCH_3)_5](BF_4)_4$ has been reported by Wilkinson.[32] The complex contains a linear Mo−O−Mo core and is diamagnetic, which shows that the antiferromagnetic coupling is stronger than in the chromium complex. However, no electronic absorption spectrum was reported.

Acid/Base Properties of the Hydroxo/Oxo Bridge. As already mentioned, the intense band at $\tilde{\nu} = 31800\ cm^{-1}$ in the absorption spectrum of $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ is characteristic of the linear $Cr^{III}OCr^{III}$ chromophore, and it is absent in a $Cr^{III}(OH)Cr^{III}$ chromophore (see Figure 1). As shown in Figure 5, ϵ of this band is high in 1.0 M aqueous $HClO_4$. The oxo bridge is apparently not protonated even in this medium, which means that the hydroxo bridge in **1** is a strong acid with the dissociation constant $K_a \gg 1$ M. The complex $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ is, however, unstable in 1.0 M aqueous $HClO_4$, and the $Cr^{III}OCr^{III}$ chromophore disappears in a first-order decay as shown in Figure 5 with a half-life of 18 s at 299 K as a result of bridge cleavage and/or substitution of MeCN ligands with water ligands followed by protonation of the oxo bridge.[33]

In "acid rhodo", the value of K_a for the hydroxo bridge has been found by Schwarzenbach[34] to be $10^{-7.63}$ M. This remarkably high acidity for a hydroxo bridge between two chromium(III) centers has been explained in terms of $d\pi - p\pi - d\pi$ overlap in the $Cr^{III}OCr^{III}$ core resulting in a delocalization of the electron lone pairs on the oxo bridge toward the metal centers.[35] This also explains the linear geometry of the core. The acidity of the hydroxo bridge in **1** is, however, more than 7 orders of magnitude higher than in "acid rhodo". This dramatic difference may have its origin in the above-mentioned possibility of *further* delocalization of the lone pairs on the oxo bridge toward the antibonding π orbitals of the $N{\equiv}C$ groups leading to a stabilization of the linear $Cr^{III}OCr^{III}$ core as a result. The MeCN ligands are thus acting as π acceptor ligands. In a series of dinuclear chromium(III) complexes $[(tpa)(X)Cr(OH)Cr(X)(tpa)]^{3+}$ [tpa = tris(2-pyridylmethyl)amine] prepared by Holwerda[36] with X = NCS^-, NCO^-, CN^-, and $N_3{}^-$, values of K_a of the hydroxo bridge fall in the range $10^{-4.25}$ to $10^{-0.64}$ M. The high acidity of the hydroxo bridge is also here explained in terms of the pyridine and X ligand π acceptor capability.

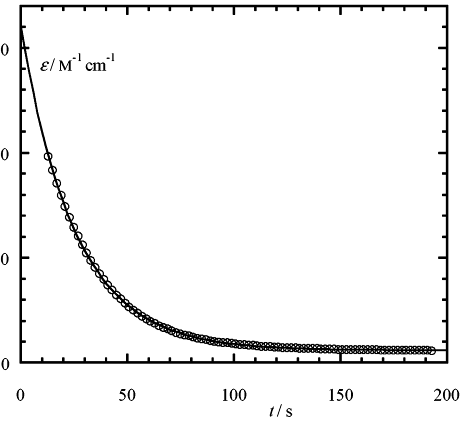

Figure 5. Molar absorption coefficient (ϵ per Cr_2) at $\tilde{\nu} = 31800\ cm^{-1}$ (λ = 314.5 nm) vs time of a solution prepared by addition of 50 μL of 4.24 × 10^{-3} M solution of $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ in MeCN to 3.00 mL of 1.0 M aqueous $HClO_4$ (T = 298.9 K). The measurement was started 13 s after mixing. The markers (○) represent observed values of $\epsilon(t)$, and the curve represents a least-squares fit of the expression $\epsilon(t) = (\epsilon_0 - \epsilon_\infty)\exp(-kt) + \epsilon_\infty$ with the values of k, ϵ_0, and ϵ_∞ being 0.03922(9) s^{-1}, 16110(33) $M^{-1}\ cm^{-1}$, and 571(3) $M^{-1}\ cm^{-1}$, respectively. At other wavelengths in the near-UV and UV range, a similar behavior was observed with values of ϵ_0 in agreement with the absorption spectrum in Figure 1b.

Conclusion

This work represents a study of the influence of the nature of the ligand L on the spectral and other properties of the binuclear compound $[L_5CrOCrL_5]^{4+}$. For L = CH_3CN, the antiferromagnetic coupling between the two metal centers is more than a factor of 2 stronger than for L = NH_3. Furthermore, the acidity of the hydroxo bridge in $[L_5Cr(OH)CrL_5]^{5+}$, for L = CH_3CN, is more than 7 orders of magnitude higher than for L = NH_3. Both of these observations can be attributed to the π acid properties of the MeCN ligand.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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