Table III. Emission Properties of Rhodium(III) and Iridium(III) Cyanide Complexes at 77 K[a]

complex	τ, μs	ν_{max}, μm^{-1}	$\Delta\nu_{1/2}$, μm^{-1}	ν_{0-0}, μm^{-1}
$K_3[Co(CN)_6]^b$	680	1.44	~0.44	~2.0
$K_3[Rh(CN)_6]^c$	84 ± 10	1.96[d]	0.45	2.5
$[Rh(CN)_6{}^{3-}]^e$	103 ± 10	1.85		
$[Rh(CN)_5H_2O^{2-}]^e$	~4	1.85	0.50	2.5
$K_3[Ir(CN)_6]^c$	39 ± 4	1.95	0.55	2.65
$[Ir(CN)_5H_2O^{2-}]^e$	0.8 ± 0.1	1.90	0.48	2.5

[a] Experimental uncertainties: ν_{max} and $\Delta\nu_{1/2}$, ±0.05 μm^{-1}; ν_{0-0}, ±0.15 μm^{-1}. The 0–0 transition energies were estimated from $\nu_{0-0} = \nu_{max} + 1.29\Delta\nu_{1/2}$.[13] [b] Emission spectra A measured as crystalline salts by: Mungardi, M.; Porter, G. B. *J. Chem. Phys.* **1966**, *44*, 4354. ν_{0-0} estimated by: Miskowski, V. M.; Gray, H. B.; Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 1410. [c] Sample in KBr pellet (1–4%). [d] This value is in agreement with a previous report of the emission maximum from $K_3[Rh(CN)_6]$: Wolpl, A.; Oelhrug, D. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 394. [e] Potassium salt as solution in 4/1 $MeOH/H_2O$ glass.

for the $M(CN)_5H_2O^{2-}$ photoproducts and for $Co(CN)_6{}^{3-}$. Emission from the $Co(CN)_6{}^{3-}$ ion has been assigned to the $^3T_1 \rightarrow {}^1A_1$ ligand field transition.[18] A similar assignment would be consistent with the broad Gaussian shapes of the emission bands seen for $Rh(CN)_6{}^{3-}$ and $Ir(CN)_6{}^{3-}$ as well as with the higher 0–0 energies of these latter transitions, given the larger ligand field splitting of Rh(III) and Ir(III). Luminescence lifetimes follow the descending order $Co(CN)_6{}^{3-} >> Rh(CN)_6{}^{3-} > Ir(CN)_6{}^{3-}$, consistent with the ascending values of the spin–orbit coupling constants of the central metal atom. Attempts to measure excited-state lifetimes of $Rh(CN)_6{}^{3-}$ and $Ir(CN)_6{}^{3-}$ in ambient-temperature, aqueous solutions were unsuccessful owing to the very weak emissions under these conditions.

Acknowledgment. This work was supported by the National Science Foundation through a grant to P.C.F. The rhodium and iridium used in these studies were provided on loan by Johnson-Matthey, Inc.

Registry No. $Rh(CN)_6{}^{3-}$, 19356-46-8; $Ir(CN)_6{}^{3-}$, 19356-47-9; $Rh(CN)_5(H_2O)^{2-}$, 42892-92-2; $Ir(CN)_5(H_2O)^{2-}$, 42893-00-5.

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Evidence for "Classical" Hydroxo-Bridged Polymers in Hydrolyzed Hexaaquachromium(III) Solutions

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Polymerization of hexaaquachromium(III) in aqueous solution yields hydroxo-bridged polynuclear complexes, which have been the subject of intensive studies. A dimeric species, $Cr_2(OH)_2{}^{4+}$, a trimeric species, $Cr_3(OH)_4{}^{5+}$, and two isomeric tetrameric species, $Cr_4(OH)_6{}^{6+}$, have been isolated and characterized in solution, but failure to obtain suitable crystalline salts of any of these species has prevented direct structure determinations.[2-5]

Table I. Acid Dissociation Constants of Chromium(III) Monomers and Oligomers in 1 M $NaClO_4$ at 25 °C

cation	pK_a[a]	ref
$[Cr(H_2O)_6]^{3+}$	4.29[b]	4
$[Cr(NH_3)_5(H_2O)]^{3+}$	5.18	28
$[(H_2O)_5Cr(OH)Cr(H_2O)_5]^{5+}$	1.6[c]	2
$[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$	3.68[d]	4
$Cr_3(OH)_4(aq)^{5+}$	4.35	4
$Cr_4(OH)_6(aq)^{6+}$ (isomer IA)[e]	3.53	5
$Cr_4(OH)_6(aq)^{6+}$ (isomer IIA)[e]	0.89	5
cis-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	3.5	23
cis,cis-$[(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	1.75	7
Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$	0.48	6,7
trans-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]^{4+}$	6.0	21
cis-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH_2)]^{4+}$	3.9	35

[a] pK_a = −log (K_{a1}/M), where K_{a1} is the concentration equilibrium constant. [b] p$K_a \approx$ 4.15 in 0.1 M $NaClO_4$ at 20 °C.[29] [c] Determined from kinetic data; 2 M $(Li,H)ClO_4$. p$K_a \approx$ 1.3–1.6 has recently been reported in an independent study.[24] [d] p$K_a \approx$ 3.5 in 0.1 M $NaClO_4$ at 20 °C.[29] [e] Cf. Figure 2.

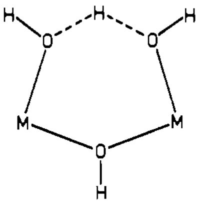

Figure 1. Hydrogen-bond stabilization of deprotonated monohydroxo-bridged "*cis,cis*"-diaqua polymers. Cf. the α-type interaction in Figure 3. This type of bond between a terminal water and hydroxide ligands is a pronounced feature in many systems,[6-8,25-27,36-39] and a $H_3O_2{}^-$-bidentate ligand has even been suggested.[36-39]

Acid-induced reaction of the blue $Cr_2(OH)_2{}^{4+}$ cation gives initially a green dimeric species, and the kinetic and thermodynamic data for the interconversion reactions between these dimers[2] are very similar to data obtained for the corresponding ammonia system, $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, and related amine systems.[6-9] This similarity suggests that the blue and green dimers are dihydroxo- and monohydroxo-bridged species, respectively, and implies that the ammine and amine hydroxo-bridged polynuclear systems[6-21] can be used as models for the polynuclear aqua

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(1) (a) Royal Veterinary and Agricultural University. (b) University of Copenhagen.

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(16) Preliminary kinetic data for the depolymerization reactions are also quoted as evidence for the proposed structures in ref 4. The data for the tetramer mixture and the trimer are, however, values for only one hydrogen ion concentration, and it is at present unresolved whether the given values correspond to true rate constants or should be conceived as composite terms. Even without this reservation, it is not made clear why a difference in half-lives between ≈7 days for the dimer and ≈21 days for the trimer should be considered so different values as to indicate a completely different structure and reactivity of these two polymers.

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0020-1669/85/1324-3496$01.50/0

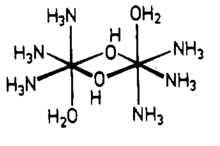

Figure 2. "*trans*"-Diaqua isomer of the dihydroxo-bridged dimer obtained by condensation of *fac*-triamminetriaquachromium(III). This isomer has $K_{a1} \approx 1.0 \times 10^{-6}$ M, whereas the otherwise analogous "*cis*" isomer is a significantly stronger acid with $K_{a1} \approx 1.3 \times 10^{-4}$ M.[35]

ion systems.

This aspect appears not to have been considered in a recent account[4,5] of possible structures of the higher aqua ion polymers, and rather unorthodox solution structures for chromium(III), involving coordination of a single hydroxide ligand to three and four metal centers, were proposed. This is in sharp contrast to the well-established structures[10-15] for otherwise analogous ammine and amine complexes and has motivated the present critical assessment.

The exclusion of the more "classical" structures was based, essentially, upon two facts.[16] First, the interconversion kinetics[5] between two isomeric tetramers was considered to be unusually rapid, and second, the acidity of the trimer[4] was significantly lower than that expected by extrapolation from data for the monomer and the dimer (cf. Table I). The latter point was taken as evidence for the presence of another and more acid water ligand type in the monomer and the dimer that was not present in the trimer. For monomeric complexes it is well-known that a trans hydroxide ligand is more effective in reducing the acidity of a coordinated water ligand than a cis hydroxide ligand.[22] Generalizing from this observation, and assuming the effect of a bridging hydroxide ligand to be similar to that of a nonbridging hydroxide ligand, it was argued[4] that the trimer should have a structure with all water ligands trans to bridging hydroxide ligands. This argumentation is seen to rest heavily upon two assumptions: first, that it is the trimer acidity which is abnormal compared to that of the monomer and dimer and, second, that effects specific for polymeric systems are less important than geometric effects in the individual subunits of the polymers.

The acid strength of terminally bound water in polynuclear complexes is often influenced *strongly* by intramolecular hydrogen-bond formation.[6-9,25-27] For dimeric complexes[6-8,23] of the type $[(X)L_4Cr(OH)CrL_4(OH_2)]^{5+}$ ($L_4 = (NH_3)_4$ or $(en)_2$ and $X = H_2O$ or NH_3; en = 1,2-ethanediamine) a significant acidity and a large variation in the first acid dissociation constant with K_{a1} from 3.2×10^{-4} to 0.33 M have been attributed to different degrees of stabilization of the deprotonated form by an intramolecular hydrogen bond as shown in Figure 1. The importance of this type of interaction is further evidenced by the data[2,24] for the monohydroxo-bridged green aqua ion dimer, which has $K_a \approx 2 \times 10^{-2}$ M. Similar properties have been found for monohydroxo-bridged complexes of rhodium(III)[25,26] and iridium(III),[27] and the interpretation has been substantiated by the crystal structure of the iridium(III) dimer: Δ,Λ-$[(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)]_2(S_2O_6)_3(ClO_4)_2{\cdot}3H_2O$.[27] Clearly, these significant effects cannot be ignored in a comparison of acidities of the aquachromium(III) polymers.

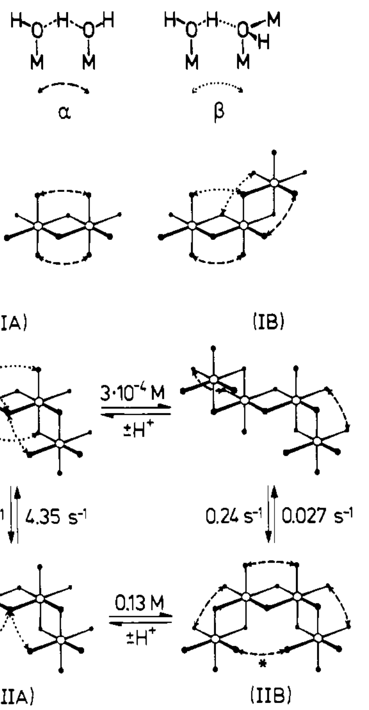

Figure 3. Suggested stabilization of aquachromium(III) polymers by intramolecular hydrogen bonds between terminal water ligands and terminal hydroxide ligands (α type, - - -) or bridging hydroxide ligands (β type, ···). β-Type interactions in the tetramers at the lower part of the figure are only shown in the acid forms at the left, but may of course also take place in the deprotonated forms at the right. These deprotonated forms contain only *one* terminal hydroxide ligand, and therefore only *one* of the suggested α-type interactions is operative in each polymer. Comparison between the stabilizations of the deprotonated forms of mono-hydroxo- and dihydroxo-bridged systems indicates not unexpectedly a greater hydrogen-bond stabilization in the more flexible monobridged system (cf. Table I). The significant acidity of the IIA tetramer is therefore most readily explained by stabilization of the deprotonated IIB isomer by the asterisk-marked α-type hydrogen bond.

The statistically corrected water ligand acidity[4,28,29] of hexaaquachromium(III) is only slightly larger than that of the pentaammineaquachromium(III) ion (cf. Table I). In the dihydroxo-bridged systems, however, the aqua ion dimer with $K_a \approx 2 \times 10^{-4}$ M is a significantly stronger acid than that of the

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(23) *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ has $pK_a = 2.8$ in 0.14 M $NaClO_4$ at 20 °C (see ref 17). In 1 M $NaNO_3$ the value is 3.5 at 25 °C (private communication from Dr. P. Andersen, Department of Inorganic Chemistry, University of Copenhagen).

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(28) Mønsted, O., unpublished results.

(29) Meyenburg, U.; Široký, O.; Schwarzenbach, G. *Helv. Chim. Acta* **1973**, *56*, 1099.

(30) In this context it is important that similar interactions between coordinated ammonia and bridging hydroxide have been observed in crystal structures of trimeric and tetrameric hydroxo-bridged chromium(III) ammines.[11,13] The fact that coordinated water is a much stronger acid than coordinated ammonia would suggest that a similar effect should be even more pronounced in the chromium(III) aqua systems. Equilibrium data for the stepwise polymerization processes

$$Cr_{n-1}(OH)_{2n-4}{}^{(n+1)+} + Cr(OH)_2{}^{+} \overset{K_n}{\rightleftharpoons} Cr_n(OH)_{2n-2}{}^{(n+2)+}$$

are $K_2 \approx 1 \times 10^5$ M^{-1}, $K_3 \approx 6 \times 10^6$ M^{-1}, and $K_4 \approx 2 \times 10^5$ M^{-1}. The slightly greater stability of the trimer does not require a different structure for this species, but can readily be explained by β-type interactions in the present structures. From Figure 3 it may thus be noted that the dimer and trimer are stabilized by 0 and 2 β-type interactions, respectively, whereas the effective number of such interactions in the dominating IA tetramer, because of geometric distortions, most likely is somewhere between 2 and 3. This crude correlation suggests that a stabilization energy about 5 kJ mol^{-1} is associated with each effective β-type interaction, which seems a reasonable number.

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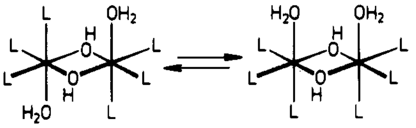
(34) Wieghardt, K.; Schmidt, W.; Nuber, B.; Prikner, B.; Weiss, J. *Chem. Ber.* **1980**, *113*, 36.

Scheme I



dimers[21,35] obtained by polymerization of *fac*-triamminetriaquachromium(III), shown in Figure 2, which has no possibilities for formation of a hydrogen bond of the type shown in Figure 1. As shown in the upper part of Figure 3, "novel" features therefore need not be involved to account for the aqua ion dimer being more acid than the trimer: The dimer and the trimer have increased acidity caused by hydrogen-bond stabilization of their deprotonated forms, the trimer is less acid than the dimer by a similar stabilization of the acid form, and the acidity-strengthening effect is smaller in these dihydroxo-bridged systems than in the more flexible monohydroxo-bridged systems.

The thermodynamic and kinetic data for the two aqua ion tetramers can be rationalized analogously, and the lower part of Figure 3 shows a suggestion in agreement with the chromium-51 isotopic labeling experiments[4] and "classical" bonding modes within chromium(III) polymer chemistry as demonstrated[10] by the structure of one of the $[Cr_4(en)_6(OH)_6]^{6+}$ isomers (en = 1,2-ethanediamine). The significant acidity of polymer IIA is caused by an effective stabilization of the deprotonated form IIB by an intramolecular hydrogen bond between terminally bound water and hydroxide. A similar interaction in an equally flexible system is not possible in the deprotonated form, IB. The stability of the protonated form IA relative to IIA may be rationalized in terms of a destabilization of IIA caused by replusion between the two terminally bound aqua ligands (cf. Figure 3) and by stabilization of IA by intramolecular hydrogen bonds between terminally bound water and bridging hydroxide. In the latter type of interaction a terminally coordinated water donates hydrogen to bridging hydroxide and it is seen that the number of such interactions in IA may be larger than in IIA.[30]

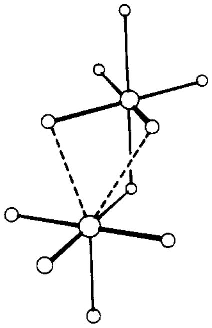


Figure 4. Suggested idealized transition-state structure for the "bridge-shift" reactions; see the text.

To summarize, it seems that the thermodynamic stability of IA in acid solution and of IIB at higher pH and also the "anomalously" high acidity of IIA can be rationalized in a semiquantitative way through two types of intramolecular hydrogen-bond interactions with terminally bound water donating hydrogen to either a terminally bound or a bridging hydroxide ligand.

The suggested interconversion processes in Figure 3 are similar to the "cis/trans" isomerization reactions in other dihydroxo-bridged systems (Scheme I), which for both cobalt(III) and rhodium(III) and a variety of ligands, L, have enhanced rate constants.[31-34] The generally accepted associative character of substitution reactions at a chromium(III) center easily accommodates these bridge-shift reactions, as shown in Figure 4. The proximity of the "entering ligand" to the bridge should be noted, and it is also relevant to point out that this reaction type may take place without the intermediate formation of a singly bridged species. The proposed mechanism should be valid for dihydroxo-bridged species with a water ligand in cis position to the double bridge and has recently been demonstrated to occur for the chromium(III) dimer in Figure 2.[35] It should also take place in the aqua ion dimer and trimer, but it is readily seen that this type of reaction cannot be monitored by conventional UV–vis spectrophotometry for the latter two species.

In summary, structures other than those presented in ref 4 and 5 are consistent with the properties of the polynuclear Cr(III)–aqua species, but the present experimental data do not permit unambiguous structural assignment. The structures proposed in the present paper are consistent with established structures of other chromium(III) systems and provide a reasonable explanation for the kinetic and thermodynamic properties. Hence, the introduction of unorthodox structures to explain the observations is not warranted.

Acknowledgment. Our thanks are due to Dr. P. Andersen of the Department of Inorganic Chemistry at the University of Copenhagen for permission to quote his recent data prior to publication.[35]

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(35) Both "*trans*"- and "*cis*"-$[(H_2O)(H_3N)_3Cr(OH)_2Cr(NH_3)_3(OH_2)]^{4+}$ (cf. Figure 2) have recently been isolated in solid crystalline salts. Kinetic data for the equilibration process between the two species are qualitatively similar to the tetramer equilibration data in ref 5. The cis isomer is a significantly stronger acid than the trans isomer,and at intermediate hydrogen ion concentrations the "*cis*"-aquahydroxo species is dominating at equilibrium: Andersen, P. *Acta Chem. Scand., Ser. A*, in press.

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Additions and Corrections

1985, Volume 24

H.-P. Abicht, J. T. Spencer, and J. G. Verkade*: Optical Resolution of "Weakly Chiral" $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)$.

Page 2132. Reference 4 is incorrect. It should be: Szafraniec, L. J.; Szafraniec, L. L.; Aaron, H. S. *J. Org. Chem.* **1982**, *47*, 1936.—J. G. Verkade