d–d gap in my notation) while in the carbonyls the HOMO is at the s–d gap and is the $A_{2g}(1)$ orbital ($\bar{F}_d^{\delta}$ in TSH notation), which lies above the M–M antibonding levels of d-orbital parentage that are partially hybridized with ligand orbitals.

Similarly, in the edge-bridged M_6X_{12} structure (e.g. M = Nb, Ta, Pt, X = Cl) the eight M–M bonding orbitals that remain below the d–d gap are[2,3]

$$A_{1g}(2),\ S_d^{\sigma};\ T_{1u}(1),\ P_d^{\pi};\ T_{2g}(1),\ D_d^{\pi};A_{2u}(1),\ F_d^{\delta}$$

Of course, it is not suggested that these levels are identical with the corresponding levels in the bare M_6 cluster; there will be some interaction with ligand orbitals that can only be quantified by accurate calculation. The schematic Figure 4 of ref 3 shows these levels to be M–M bonding but raised somewhat in energy as compared with the bare M_6 cluster. With this notation established, we can contrast the above description[2,3,14] with that offered for trigonal-bipyramidal $(FeX_3)_5^{2-}$ (X = H),[1] which is consistent with my general account of bonding in metal-cluster compounds except in one respect, namely the proposed three-orbital/four-electron interaction ($L_d^{\pi}/L_X^{\pi}/L_p^{\pi}$; L = P, D, ... in the TSH notation).

There are several things that can be said about this description; first, it might be argued that tbp $(FeX_3)_5^{2-}$ is quite different from the cluster species that I reviewed explicitly so there is no inconsistency; however, at the end of the note,[1] this three-orbital interaction seems to be regarded as a *general* aspect of bonding in cluster compounds. This is surely contentious; the hexanuclear species referred to above and described in detail earlier[2,3,14] are obvious counterexamples—in particular, the P_d^{π}, D_d^{π} levels (i.e. $T_{1u}(1)$ and $T_{2g}(1)$, respectively) in these species are *not* strongly mixed with metal p orbitals because of a ligand polyhedron induced interaction. The accurate calculations that I referred to[2,3] show that, for example, in octahedral $M_6(\mu_3\text{-}X)_8X_6$ the ligand polyhedron $t_{2g}(2)$ orbitals hybridize strongly with the metal-cluster M–M *antibonding* d-orbital levels $T_{2g}(2)$ ($=\bar{D}_d^{\pi}$) *and* the metal cluster p-orbital level $T_{2g}(3)$ ($=P_p^{\pi}$). In my view, the proposed three-orbital interaction is a result of the extended Hückel parameterization and cannot be taken as a general feature of the bonding in ligated metal clusters.

Very recent calculations on tbp $Fe_5(CO)_{15}^{2-}$ and $Ru_5(CO)_{15}^{2-}$ using a modified Fenske-Hall SCF program[17] suggest that the S_s^{σ} skeletal orbital is the HOMO in these cluster species and that it is stabilized somewhat by interactions involving the carbonyl π/π^* levels—tangential orbitals not referred to in simple isolobal arguments. In the general case the fate of the metal cluster S_s^{σ} orbital is not as clear-cut as is implied in ref 1. Although it is well established that the actual ligand polyhedron is not electronically demanding as far as the distribution of cluster *molecular orbitals* is concerned[15,16] (for example, hexanuclear cluster carbonyls generally obey the 86-electron rule irrespective of ligand count), this does *not* imply a similar invariance of the *atomic orbital* makeup of the cluster molecular orbitals.[18] Thus, it should be noted that the S_s^{σ} orbital has no bonding role in cluster carbonyl species such as $Co_6(CO)_{14}^{4-}$, $Ni_6(CO)_{12}^{2-}$, and $Pt_6(CO)_{12}^{2-}$,[6,8] and yet all of these, like $Os_6(CO)_{18}^{2-}$ (for which S_s^{σ} may well be the HOMO), satisfy the $7n + 1$ rule for the number of occupied molecular orbitals. In the Ni_6 and Pt_6 cluster carbonyls, an in-phase combination of carbonyl $2\pi^*$ orbitals is pulled down to form the HOMO of the dianions, and the metal-derived S_s^{σ} orbital lies *above* the carbonyl $2\pi^*$ band of levels.[6,8] The simple TSH bonding scheme for M_n and M_nX_x clusters at the end of ref 1 is surely overstated; it may be valid for some cluster compounds, but it can hardly be the general result claimed. Of course, all bonding schemes need to be confronted by experimental data; estimates of metal-cluster d bandwidths from a variety of methods have recently been compared[19] with experimental photoelectron spectroscopy,[13,20] and chemical pseudopotential calculations on Os and Pt clusters[8,21] agree well with their solution visible/UV spectra (albeit that the spectra are of low resolution).[22] Such comparisons provide concrete evidence to justify pursuing approaches to cluster chemistry that utilize the experience gained in transition-metal physics in conjunction with existing chemical knowledge.

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Solubility of Chromium(III) Hydroxides

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In a recent publication Rai et al.,[1] having recognized the lack of quantitative information concerning the precipitation/dissolution of chromium(III) hydroxides, reported results of solubility measurements designed to further the understanding of these processes. Suspensions of chromium(III) hydroxides were prepared (pH range 4–14) and equilibrated with stirring at room temperature (22 ± 2 °C) for periods of between 6 and 134 days. The total Cr content of the liquid and solid phase was determined after filtration through Amicon Type F-25 centriflo membrane filters (0.0018 μm median pore size). The resultant solubility curve was parabolic with regions of high solubility at low (<6) and high (>10) pH. In analyzing these results, Rai et al.[1] found that their data could best be described by a series of equilibria involving three major monomeric solution species, viz. $CrOH^{2+}$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$. Consequently, it was concluded that (i) Cr^{3+} and $Cr(OH)_2^+$ were present only in trace concentrations and (ii) polynuclears[2] (e.g. $Cr_2(\mu\text{-}OH)_2^{4+}$ and $Cr_3(\mu\text{-}OH)_4^{5+}$) were absent even at elevated temperatures. However, Rai et al.'s solubility data does not totally disprove the presence of Cr^{3+} and $Cr(OH)_2^+$, since the preferred three-parameter fit is only marginally better than a five-parameter fit allowing for their presence.[3] More importantly, the technique employed to measure $Cr(OH)_3$ solubilities[1] is *sensitive to the charge and not to the nuclearity* of soluble solution species;[3] e.g., $CrOH^{2+}$ is indistinguishable from the deprotonated binuclear $Cr_2(\mu\text{-}OH)_2(OH)_2^{2+}$. In the discussion to follow, existing[4–8,11–15] and new information will be used to demonstrate the importance of hydrolytic polymerization in equilibrating suspensions of chromium(III) hydroxides. Furthermore, chromium(III) hydroxides prepared as described by Rai et al.[1] will be shown to consist, almost entirely, of polynuclears.

Results and Discussion

Solubility and Composition of Chromium(III) Hydroxides. For Rai et al.'s equilibrated suspensions[1] $[Cr(III)]_T$ (total Cr(III) concentration in solution) decreased from ca. 0.02 M at pH 4 to ca. 10^{-4} M at pH 5. However, on the basis of the solubility constants of Schwarzenbach and co-workers,[4] determined for fresh precipitates of the "active" chromium(III) hydroxide, a decrease in $[Cr(III)]_T$ from 2.41 to 0.012 M is expected over the same pH range. Solubility measurements undertaken here were in agreement with these predictions. For instance, ultrafiltration of suspensions prepared by mixing solid samples of the "active" hydroxide with a pyridine/$HClO_4$ mixture (total $[Cr(III)]$ = 0.02 M) and equilibrated for 1 day with stirring, gave $[Cr(III)]_T$ = 0.016 and 0.013 M at pH 4.90 and 5.04, respectively. The

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somewhat higher solubilities when compared with those calculated from the data of Schwarzenbach and co-workers[4] are due to the formation of oligomers with low nuclearity during equilibration.[5] Nevertheless, the solubility of the "active" hydroxide in the pH range 4–5 is ca. 100-fold greater than that of Rai et al.'s $Cr(OH)_3$.[1] This dramatic difference in solubility cannot be ascribed solely to time-dependent changes in crystallinity of the "active" hydroxide since its structure, based on an octahedral layer in which $Cr(OH)_3(OH_2)_3$ units are linked exclusively through H-bonding between OH^- and H_2O ligands of adjacent Cr(III) centers,[6] suggests rapid equilibration between solid and solution phases. A more realistic explanation is that Rai et al.'s chromium(III) hydroxides[1] consist predominantly of polynuclears that are less soluble than the "active" hydroxide.

Precipitates of $Cr(OH)_3$ were prepared under conditions identical with those described by Rai et al.,[1] viz. by alkalinization of $[CrCl_2(OH_2)_4]Cl$ with NaOH. The Cr and Cl content of these precipitates was 31.7% (±0.1%) and <0.1%, respectively. Chromatographic analysis of these materials, with techniques described elsewhere,[7] showed that they contained only a small amount of monomeric Cr(III) (ca. 1.3%), with the remainder consisting of polynuclears. In marked contrast, the "active" chromium(III) hydroxide was shown to contain ca. 99% of monomeric Cr(III).[7] These dramatic differences in composition can be ascribed to the use of different precipitation conditions:

(i) Rai et al.'s[1] precipitation of $Cr(OH)_3$ involved the addition of strong, concentrated base (0.67 M Et_4NOH or 10 M NaOH) to concentrated (1.5 M) Cr(III) solutions. These conditions favor the formation of a polymeric material. Polymerization is very sensitive to [Cr(III)] as it involves a second (or higher) order process whose rate increases markedly with [Cr(III)]. Moreover, unless stirring is extremely efficient and the addition of base carefully controlled during precipitation, localized regions of high base concentration can occur. Cr(III) species coming into direct contact with these high base concentrations can undergo rapid polymerization. In strongly alkaline solution (pH ~14), deprotonation of Cr^{3+} is reported to form monomeric chromites, e.g. $Cr(OH)_4(OH_2)_2^-$, which are rapidly transformed into polynuclears.[8] As a consequence, acidification of these solutions does not quantitatively regenerate Cr^{3+} (violet) but instead gives a green solution containing several oligomers and very little Cr^{3+}.

(ii) For the major part of the equilibration studies,[1] $[CrCl_2(OH_2)_4]Cl$ was used as a source of Cr(III) in the precipitation of $Cr(OH)_3$. This complex, however, contains bound chloride, which has the effect of labilizing the coordination sphere of Cr(III) (e.g. the exchange of H_2O trans to Cl on $CrCl^{2+}$[9] is ca. 15-fold faster than on Cr^{3+}[10]), possibly leading to accelerated intramolecular substitution (or polymerization) with concurrent release of H_2O or Cl^-. The $Cr(OH)_3$ precipitates prepared here contain no Cl^-, which suggests that it was released in preference to H_2O or OH^-. This behavior is not uncommon in the chemistry of Cr(III). For example, the formation of monodispersed sols of Cr(III) by alkalinization and aging of either chromium alum or $Cr_2(SO_4)_3 \cdot nH_2O$ occurs with quantitative release of SO_4^{2-}.[11]

The dissolution mechanism of polymeric $Cr(OH)_3$ is complicated since, in principle, any of the polynuclears present can equilibrate between the solid and the solution phases. Furthermore, dissolution can be assisted by either protonation (low pH) or deprotonation (high pH). It could be argued that monomeric Cr(III) species can be generated by selective cleavage of polynuclears and that the interpretation of the $Cr(OH)_3$ solubility in terms of mononuclears is still valid. However, over the pH range studied the cleavage of polynuclears would be expected to be extremely slow; e.g., work in progress on the cleavage of the hydrolytic dimer[12] indicates that $t_{1/2}$ is ca. 250 days in the pH range 2–5. Furthermore, even if cleavage does take place there is no guarantee that it would lead exclusively to mononuclears. Studies on Cr(III) oligomers showed that the tetramer cleaved into equal amounts of trimer and monomer[2] while the hexamer gives exclusively trimer[13] (subsequent cleavage of trimer was much slower[2]). Given the observed change in cleavage site from a terminal to a central Cr atom in going from tetramer to hexamer, one cannot be sure that the cleavage of polymeric $Cr(OH)_3$ would produce only monomeric solution species.

Aging of Chromium(III) Hydroxides. Rai et al.[1] did not identify the species present in solution and/or solid phase of equilibrated $Cr(OH)_3$ suspensions, despite the availability of a suitable analytical method.[14] This chromatographic method has allowed investigations of the chemical changes associated with the polymerization of Cr^{3+} in homogeneous solution (pH <5)[15] and the aging of "active" chromium(III) hydroxide suspensions (5 < pH < 11).[14] It is based on the fact that on acidification of the aged mixtures (pH ~2), polynuclears formed during aging are stable to acid cleavage and can be isolated and determined individually, while any unreacted mononuclears instantaneously regenerate Cr^{3+}. This method was, therefore, used to determine the composition of solid and solution phases of aged suspensions of $Cr(OH)_3$, itself prepared as described by Rai et al.[1]

Addition of $Cr(OH)_3$ (0.25 g) to a mixture of 0.1 M pyridine/0.08 M $HClO_4$ (10 mL) gave a suspension with pH 4.30 after an aging period of 6 days at 23 ± 3 °C. Under these conditions, $[Cr(III)]_T = 1.7 \times 10^{-3}$ M in agreement with Rai et al.'s value for a similar aging period. Chromatographic analyses indicated that the solid phase consisted almost exclusively of polynuclears (> 99%) while the liquid phase contained 8% monomeric Cr(III) and 92% polynuclears. *Thus, although the liquid phase was somewhat enriched in monomeric Cr(III) species, it nevertheless consisted predominantly of polynuclears.*

These results for low I (≤0.1 M) are consistent with results from previous work at higher I (ca. 1 M).[14,15] In these experiments it was shown that extensive polymerization of both solutions and suspensions of mononuclear Cr(III) occurred, even after the shorter aging periods of ≤3 days. For example, a stirred suspension of "active" chromium(III) hydroxide with [Cr(III)] = 0.02 M at pH 5.05 contained only 3.3% mononuclears after 16 h of aging[14] while a homogeneous solution with [Cr(III)] = 0.02 M at pH 4.81 contained only 1.4% mononuclears after 23 h aging.[15] Experiments undertaken here show that polymerization also occurs during aging of the "active" chromium(III) hydroxide at lower I: (i) A suspension prepared by mixing equal volumes of Cr^{3+} (0.044 M) with pyridine (0.18 M) and aged with stirring for 16 h (pH 5.14; I ≤0.13 M) contained 31% mononuclears and 69% polynuclears. (ii) A suspension prepared by adding solid "active" chromium(III) hydroxide to a mixture of 0.1 M pyridine/0.08 M $HClO_4$ ([Cr(III)] = 0.02 M; pH 4.90; I ≤0.14 M) contained 30% mononuclears and 70% polynuclears after 24 h of aging with stirring; the liquid phase consisted of 64% polynuclears and 16% mononuclears while the solid phase was made up of 6% polynuclears and 14% mononuclears.

Conclusion

Chromatographic analyses of Rai et al.'s[1] $Cr(OH)_3$ have shown

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that this material is, almost entirely, polymeric. Thus, the solubility measurements[1] are complicated by the possibility that any of the polynuclear species, in addition to mononuclear species, can equilibrate between solid and solution. As a consequence, the liquid phase of equilibrated $Cr(OH)_3$ suspensions consists predominantly of polynuclear species. Thus, their mononuclear-based model gives a misleading and oversimplified view of chromium(III) hydroxide precipitation/dissolution reactions. This example emphasizes the dangers associated with the interpretation of thermodynamic and/or kinetic data in systems where all species are not fully identified.

Although information is available on the various deprotonated forms of Cr^{3+}[4] and on the lower Cr(III) oligomers (dimer–hexamer) and their deprotonated forms,[2] a number of higher oligomers, yet to be isolated and characterized, have also been observed.[8] The current lack of information about these higher oligomers and their deprotonated forms precludes reinterpretation of Rai et al.'s solubility data[1] with a more realistic equilibrium model.

Registry No. $Cr(OH)_2^+$, 67588-88-9; $CrOH^{2+}$, 15906-92-0; Cr^{3+}, 16065-83-1; $Cr(OH)_3$, 1308-14-1.

Additions and Corrections

1987, Volume 26

Nancy J. Christensen, Allen D. Hunter, Peter Legzdins,* and Luis Sánchez: Reduction of $[(\eta^5\text{-}C_5H_5)M(NO)I_2]_2$ (M = Mo, W) Dimers by PMe_3: Synthesis and Properties of the Novel Complexes $M(NO)(PMe_3)_4I$.

Page 3345. Reference 6 was incorrect and should be as follows: James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1971**, 1068.—Peter Legzdins