Table III. Fractional Coordinates and Isotropic Thermal Parameters for **6**

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
P	3937 (1)	2377.5 (8)	7027 (1)	20.5 (2)
N1	3692 (4)	1162 (3)	7935 (4)	27.0 (7)
N2	3178 (4)	1516 (3)	5178 (4)	27.7 (7)
N3	4033 (3)	3606 (3)	6090 (4)	23.6 (6)
N4	3161 (4)	3361 (3)	8506 (4)	25.1 (7)
C1	3378 (5)	18 (4)	6523 (5)	34.4 (9)
C2	2547 (5)	399 (4)	5105 (6)	36 (1)
C3	2752 (5)	2060 (4)	3858 (5)	35 (1)
C4	3772 (5)	3056 (4)	4220 (5)	34.1 (9)
C5	3027 (4)	4624 (3)	6806 (5)	28.6 (8)
C6	3036 (5)	4643 (3)	8588 (5)	28.1 (9)
C7	2779 (5)	2979 (4)	9817 (5)	32.8 (9)
C8	2553 (5)	1620 (4)	9012 (5)	33.0 (9)
C9	2509 (5)	−3487 (4)	13562 (5)	30.8 (9)
C10	948 (5)	−3746 (5)	13228 (7)	45 (1)
O1	3300 (3)	−4410 (3)	13087 (5)	42.2 (8)
O2	2810 (4)	−2437 (3)	14196 (6)	64 (1)
F1	473 (5)	−4125 (6)	11619 (6)	109 (2)
F2	655 (4)	−4566 (4)	13764 (7)	152 (1)
F3	121 (4)	−2830 (5)	13747 (7)	111 (2)
C11	3142 (5)	8322 (4)	−259 (6)	37 (1)
C12	1551 (6)	8231 (5)	−712 (8)	50 (1)
O3	3593 (4)	9314 (3)	698 (5)	49.6 (9)
O4	3840 (5)	7416 (4)	−888 (7)	81 (1)
F4	966 (4)	8917 (4)	−1580 (6)	95 (1)
F5	1103 (5)	7182 (4)	−1460 (10)	138 (2)
F6	924 (5)	8669 (7)	630 (6)	141 (2)

The P–H17 bond lengths are similar in **6** and **2** and very short as expected in the equatorial plane of a trigonal bipyramid.

Differences between the structures of **6** and **2** are observed when examining the conformations of the five-membered rings. A schematic view of **6** and **2** along the N1–P–N3 axis (Figure 3) shows an "8" pattern for **2** and an "S" pattern for **6** (note in the latter case the eclipsed positions of the cycles in the foreground and background of the equatorial plane containing atoms P, N4, N2, and H17).

Experimental Section

Instrumentation. NMR spectra were obtained on a Bruker WH-90 spectrometer (chemical shifts are given in ppm downfield from external Me$_4$Si for ^{13}C, from external 85% H_3PO_4 for ^{31}P, and from internal CCl_3F for ^{19}F). Infrared spectra were recorded on a Bruker IFS 45 spectrophotometer. Mass spectra were obtained on a R 10 Ribermag L 10 instrument. Molar conductances were determined with a Tacussel CD6NG electronic conductometer.

Synthesis of Cyclenphosphorane–Bis(trifluoroacetic acid) (6). A 0.123-mL portion (1.66 mmol, Aldrich) of trifluoroacetic acid was added to a solution of 0.162 g (0.81 mmol) of cyclenphosphorane (**1**)[7] in 5 mL of CH_2Cl_2 at −40 °C. A white precipitate was formed immediately. It was filtered and washed repeatedly with CH_2Cl_2, yielding 0.309 g (90%) of a white hygroscopic powder soluble in CH_3CN. Anal. Calcd for $C_{12}H_{19}N_4O_4F_6P$: C, 33.67; H, 4.47; N, 13.09; P, 7.24. Found: C, 33.73; H, 4.50; N, 13.17; P, 6.93. ^{1}H NMR (CD_3CN): δ 11.9 (0.5 H,[11] H–P), 10.6 (2 H, H–N$^+$), 3.2 (m, 16.5 H). ^{31}P NMR (CH_3CN): δ −48.0 (d, $^1J_{PH}$ = 780 Hz). ^{13}C NMR (CD_3CN): δ +44.5 (d, $^2J_{CP}$ = 7 Hz), +42.7 (d, $^2J_{CP}$ = 13 Hz). IR (KBr pellet, cm^{-1}): ν(N–H) 2806 (w), ν(P–H) 2450 (w), ν(CO) 1678 (s).

Synthesis of Cyclenphosphorane–Tetrafluoroboric Acid (7). A solution of tetrafluoroboric acid (54%) (0.08 mL, 1.2 mmol, Fluka) in Et_2O was added to 0.24 g (1.2 mmol) of **1** in 5 mL of CH_2Cl_2 at −35 °C. The solution was allowed to warm to room temperature. Evaporation then led to a gummy product, which was taken up in 50 mL of Et_2O with stirring overnight. Filtration yielded 0.28 g (83%) of a white, slightly hygroscopic product, soluble in toluene, CH_2Cl_2, and CH_3CN. ^{1}H NMR (CD_2Cl_2): δ 11.4 (0.5 H,[11] H–P), 6.7 (s, 1 H, H–N$^+$), 2.9 (m, 16.5 H). ^{31}P NMR (CH_3CN): δ −47.7 (d, $^1J_{PH}$ = 700 Hz). ^{13}C NMR (CD_3CN): δ +44.2 (d, $^2J_{CP}$ = 8.8 Hz). ^{19}F NMR (CH_2Cl_2): δ −152 (s). IR (KBr pellet, cm^{-1}): ν(P–H) 2375 (w). Molar conductance (10^{-3} *m* in acetone): 116 Ω^{-1} cm^2 mol^{-1}.

Synthesis of Cyclenphosphorane–Methyl Iodide (8). One molar equivalent of MeI (0.024 mL, 0.38 mmol, Aldrich) was added to a solution of **1** (0.077 g, 0.38 mmol) in 5 mL of CH_2Cl_2 with stirring at room temperature. The reaction mixture remained clear. Evaporation of the solvent led quantitatively to 0.131 g of a white hygroscopic powder. Anal. Calcd for $C_9H_{20}N_4PI$: C, 31.59; H, 5.89; N, 16.37; P, 9.05. Found: C, 31.20; H, 5.70; N, 16.40; P, 8.93. ^{1}H NMR ($CDCl_3$): δ 10.9 (0.5 H,[11] H–P), 3.0 (m, 16.5 H), 2.65 (d, 3 H, $^3J_{HP}$ = 10 Hz). ^{31}P NMR (CH_2Cl_2): δ −21.2 (d, $^1J_{PH}$ = 740 Hz). ^{13}C NMR (CD_2Cl_2): δ 52.1, 51.7, 45.4, 45.2, 44.7, 43.8, 42.0, 41.7, 40.6, 40.3. IR (KBr pellet, cm^{-1}): ν(P–H) 2400 (w). MS (chemical ionization with NH_3, *m/e*): (M − I)H$^+$ (91%), (M − MeI)H$^+$ (100%).

Crystal Structure. Suitable colorless platelike crystals were obtained from a saturated solution of **6** in CH_3CN cooled to −30 °C. These crystals are triclinic and belong to space group $P\bar{1}$. The unit cell parameters given in Table I have been refined by least squares from angular positions of 25 reflections.

The intensities of 2930 reflections were collected with an Enraf-Nonius CAD4 automated diffractometer. A variation of 2.1% in the intensity of the standard reflections recorded periodically was observed during the data collection. The data were corrected for Lorentz and polarization factors but not for absorption. The atomic scattering factors were taken from Cromer and Waber.[12] The structure was solved by direct methods (MULTAN).[13] Fourier synthesis allowed the location of all non-hydrogen atoms. All programs used were from the SDP program library.[14] The hydrogen atoms were located from difference Fourier synthesis or were placed in calculated positions on their parent carbons (C–H = 0.96 Å). They were introduced isotropically but not refined (B = 5 Å^2). Convergence of the full-matrix least-squares refinement gave residuals R = 0.067 and R_w = 0.102. In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$.

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Supplementary Material Available: Positional parameters of hydrogen atoms (Table A) and thermal parameters (Table B) (2 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(11) $^1J_{H-P}$ and δ_{H-P} cannot be determined from the ^{1}H NMR spectrum because the upfield branch of the doublet is masked by the signals of the methylenes. Only the chemical shift of the downfield branch is given.

(12) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(13) Main, P.; Fiske, S. J.; Hall, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *Multan 80. A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, York, England, and University of Louvain, Louvain, Belgium, 1980.

(14) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 44–71.

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Reply to "Extended Hückel Calculations and the Role of d Orbitals in Transition-Metal-Cluster Bonding"[1]

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In a recent note[1] in this journal, D. G. Evans gave a detailed presentation of some extended Hückel (EH) calculations on Fe$_5$ cluster species and used his results to comment on two earlier papers on mine[2,3] devoted to the bonding in transition–metal–cluster compounds. There is now general agreement about the importance of the metal d electrons in transition-metal-cluster

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(1) Evans, D. G. *Inorg. Chem.* **1986**, *25*, 4602.

(2) Woolley, R. G. *Inorg. Chem.* **1985**, *24*, 3519.

(3) Woolley, R. G. *Inorg. Chem.* **1985**, *24*, 3525.

bonding, and it is perhaps worth considering some more quantitative aspects of the MO energy level schemes that are now available from a variety of theoretical electronic structure methods.

EH calculations in the 1970s on transition-metal systems consistently gave d bandwidths that were much too narrow; since then *some* EH calculations have done much better in this regard due to changes in EH methodology. To account for this, I guessed[2,3] that this was due to using larger overlap integrals in the EH formula for the resonance integrals; this guess was mistaken. It has been pointed out[1] that the overlap integrals currently used in EH studies are small; for example, the Fe–Fe d–d overlap integrals in ref 1 (at $R_{\text{Fe–Fe}} = 2.53$ Å) are 0.051 or less, consistent with the typical values reported by transition-metal physicists and also consistent with values quoted in much older EH calculations.[4]

It is still the case of course that the newer EH resonance integrals in some calculations are larger than the earlier ones, and that fact deserves explanation. Evans's note[1] has made clear to me that the recent change in EH methodology has involved modification of the orbital energy parameters H_{dd} for the metal d electrons ("ionization energies"). As an example, consider the d band of octahedral Co_6 with $R_{\text{Co–Co}} = 2.5$ Å. In an early EH calculation,[4] the value $H_{dd}(\text{Co}) = -9.42$ eV was used with the extended Hückel constant K set equal to 1.5; this led to a d bandwidth of 1.1 eV. In ref 1 however, the values $K = 1.75$ and $H_{dd}(\text{Co}) = -13.18$ eV are cited as the currently accepted values.[5] If we assume that the (current) double-ζ overlap integrals are at least as large as those reported in the earlier calculation,[4] then the new resonance integrals will be enhanced by a factor of at least $(1.75/1.5) \times (13.18/9.42) = 1.63$, and this corresponds to an enhanced bandwidth of at least 1.8 eV (i.e. 1.1 eV × 1.63). For comparison, a recent chemical pseudopotential calculation[6] on octahedral Co_6 gives the d bandwidth = 2.3 eV in the bare cobalt cluster. So with this change in the d-orbital energy parameter, $H_{dd}(\text{Co})$, the EH calculated d bandwidth for Co_6 would be brought into much better agreement with the chemical pseudopotential results. We can now understand why a substantial d bandwidth is found in the recent Fe_5 cluster calculations;[1] these are based on the value of $H_{dd}(\text{Fe}) = -12.7$ eV; for comparison, Ballhausen and Gray's VSIE value[7] for the $d^{n-1}s^1$ configuration of Fe is −8.68 eV (ref 7 was the source of the cobalt data used in ref 4). Combined with an increase in K from 1.5 to 1.75, this amounts to an enhancement of the resonance integrals between d orbitals (and hence also an enhancement of the d bandwidth) by a factor of 1.7 as compared with the earlier EH parameterization.

While this can be a successful strategy for the cluster species of the 3d metals, it is important to appreciate that this move is *not* reliably effective for the heavier transition metals, for which EH theory may still be deficient regarding d-orbital interactions, nor is it possible for bulk metal and metal surface calculations required for chemisorption studies. Recent chemical pseudopotential calculations[8] on the $[Pt_3(CO)_6]_n^{2-}$ anions ($n = 1$–3) show d bandwidths between 4.5 and 5.5 eV, whereas EH calculations using $H_{dd}(\text{Pt}) = -13.18$ eV found a d bandwidth of about 2 eV.[9] For comparison it should be noted that photoelectron spectroscopy of salts of these platinum cluster anions on a graphite substrate show occupied d-electron levels extending over nearly 7 eV.[10,11] It is evident that the discrepancies here between EH and chemical pseudopotential calculations cannot be resolved by further lowering the H_{dd} values in the EH parameterization. It may be noted that the recommended values for the bulk metals and metal surfaces in the EH scheme[12] are close to the VSIE values for the neutral $d^{n-1}s^1$ configuration[7] and automatically give rise to band structures (and densities of states) that are only in qualitative correspondence with accurate results from band structure calculations based on the local density functional method, as Saillard and Hoffmann note explicitly.[12]

One consequence of using large negative values for the H_{dd} parameter is that the center of the d band must also be expected to occur at large negative energy values; for example, the center of the d band in the Fe_5 cluster calculation (ref 1, Figure 1) is near −12.5 eV and the band has a range of ±1.7 eV about this center. For comparison, Plummer et al.[13] give ionization energies from the d bands of small cluster carbonyls of cobalt and iron in the range 7–9 eV, i.e. some 4–5 eV lower than that suggested by a one-electron interpretation of the EH results. It may be suggested that this fairly substantial discrepancy between the experimental and theoretical values should be accounted for by electron correlation, or in other ways, but that just means that we cannot be sure of a direct correspondence between the EH orbital energy level scheme and the ground-state electronic structure, which is actually what determines the bonding. Another view is that correlation effects in clusters of this size are not that large, and the significance of the discrepancy is that the EH calculation is not good enough to allow an interpretation of the photoelectron spectroscopy.

Increasing the resonance integrals by lowering the orbital energies, H_{dd}, does not have the same effect as leaving H_{dd} unchanged (e.g. at the neutral VSIE value) and making a compensating change in the extended Hückel constant, K, because H_{dd} is also the *diagonal* matrix element for the d orbitals in the secular matrix and its value *relative* to other orbital energies is important in controlling hybridization with them. In the $Fe_5X_{15}^{2-}$ calculation (X = hydrogen) reported in ref 1, the d-orbital/ligand-donor-orbital energy separation is less than 1 eV (because the d orbital is so low) and it is hardly surprising that there are significant ligand orbital interactions with the metal-cluster d band.[1] What is surprising is the particular interaction described and the generalization based on it that is made at the end of the note.[1]

I emphasized in my papers that the d band of a bare transition-metal cluster is significantly affected by its ligand polyhedron when cluster compound formation occurs (ref 2, section 3a; ref 3, section 6, conclusion ii) and, moreover, what happens in detail, i.e. *which* d-band levels are affected, depends on the number and disposition of the ligands in the ligand polyhedron relative to the metal cluster; several examples of this feature were reviewed.[2,3] Independently, and at the same time, similar examples were discussed by Ceulemanns and Fowler[14] using a modified tensor spherical harmonic (TSH) formalism; their conclusions are essentially the same as mine. The elegant TSH model[15,16] is based on approximating the cluster as having spherical symmetry, but as Ceulemanns and Fowler point out,[14] the clarity of the TSH orbital classification can be greatly obscured by the subsequent extensive orbital mixing under the finite point-group symmetry of the actual cluster structure, and substantial reconstruction of the energy level diagram may be required.

Ceulemanns and Fowler[14] and I[2,3] show, in accordance with other literature discussions, that in the $M_6(\mu_3\text{-}X)_8X_6$ cluster species (M = Mo, X = S, Cl; M = Co, X = CO etc. with appropriate overall charges) the metal–metal *bonding* orbitals that remain *below* the d–d gap after ligation has occurred can be classified under O_h[2,3] and the TSH scheme[14] as

$$\mathrm{A_{1g}(2),\ S_d{}^{\sigma};\ T_{1u}(1),\ P_d{}^{\pi};\ T_{2g}(1),\ D_d{}^{\pi};E_g(1),\ D_d{}^{\delta};\ T_{2u}(1),\ \bar{D}_d{}^{\bar{\delta}}}$$

The difference between the sulfides and halides, and the carbonyls of this structure is that in the former these M–M bonding orbitals are the highest occupied levels (i.e. E_{HOMO} $(=\mathrm{T_{2u}}(1))$ lies at the

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(4) Mingos, D. M. P. *J. Chem. Soc. A* **1974**, 133.

(5) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(6) Bullett, D. W., private communication, 1985.

(7) Ballhausen, C. J.; Gray, H. B. *Molecular Orbital Theory*; Benjamin: New York, 1965; p 125.

(8) Bullett, D. W. *Chem Phys. Lett.* **1985**, *115*, 450.

(9) Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968.

(10) Apai, G.; Lee, S.-T.; Mason, M. G.; Gerenser, L. J.; Gardner, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6889.

(11) Woolley, R. G. *Chem. Phys. Lett.*, in press.

(12) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(13) Plummer, E. W.; Salaneck, W. R.; Miller, J. S. *Phys. Rev. B: Solid State* **1978**, *18*, 1673.

(14) Ceulemans, A.; Fowler, P. W. *Inorg. Chim. Acta* **1985**, *105*, 75.

(15) Stone, A. J. *Mol. Phys.* **1980**, *41*, 1339.

(16) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563.

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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(17) Wales, D. J., submitted for publication in *J. Chem. Soc., Dalton Trans.* and private communication.

(18) Woolley, R. G. *Nouv. J. Chim.* **1981**, *5*, 219, 227, 441.

(19) Johnson, B. F. G.; Woolley, R. G. *J. Chem. Soc., Chem. Commun.* **1987**, 634.

(20) Green, J. C.; Mingos, D. M. P.; Seddon, E. A. *Inorg. Chem.* **1981**, *20*, 2595.

(21) Bullett, D. W. *Chem. Phys. Lett.* **1987**, *135*, 373.

(22) Drake, S. R.; Johnson, B. F. G.; Lewis, J.; Woolley, R. G. *Inorg. Chem.* **1987**, *26*, 3952.

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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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