elements in the periodic table. None of the refinements using data for elements of lesser atomic number than osmium were satisfactory. In Table III and Figures 1 and 2 are given the results for refinements using phase shift data for osmium, platinum, mercury, lead, polonium, and radon. Examination of the *R* factors, [the radial distribution and molecular intensity difference curves (Figures 1 and 2)], and the errors quoted in Table III reveal that the refinement in which phase shift factors for lead were used gave the lowest *R* factors and the smallest errors.

Changing the phase shift factors has no significant effect upon the distances and angles (see Table III) but does modify the amplitudes of vibration, there being a gradual increase in the amplitudes with increase in *Z*. Unfortunately complete vibrational spectroscopic data for $\mathrm{OsOCl_4}$ are not available so we were unable to calculate reliable theoretical values for the vibrational amplitudes.

We can offer no good explanation for the results, but it would appear worthwhile to examine the effect of varying the phase shift factors when studying the structures of molecules containing atoms with a large nuclear charge.

Results and Discussion

The results obtained in our investigation of $\mathrm{OsOCl_4}$ are consistent with the molecule having C_{4v} symmetry in the gas phase. There may be very small deviations from ideal C_{4v} symmetry but C_{3v} and C_{2v} models did not give a satisfactory fit to the data. The results for $\mathrm{OsOCl_4}$ with those for $\mathrm{ReOCl_4}$,[8] $\mathrm{WOCl_4}$,[7] and $\mathrm{MoOCl_4}$[19] are included in Table I. The gas-phase structure of $\mathrm{OsOF_4}$ has been determined by electron diffraction,[20] and a value of 1.624 (25) Å was assigned to $r_\mathrm{a}(\mathrm{Os{=}O})$. Thus the value for the fluoride appears to be shorter than that for the chloride [$\Delta r_\mathrm{a}(\mathrm{Os{=}O}) = 0.037\ (28)$ Å], which is in accord with $r_\mathrm{a}(\mathrm{W{=}O})$ being shorter in $\mathrm{WOF_4}$[21] than in $\mathrm{WOBr_4}$[22] [$\Delta r_\mathrm{a}(\mathrm{W{=}O}) = 0.017\ (9)$ Å]. These differences between the fluorides and chlorides have been attributed to electronegativity effects.

For the species $\mathrm{MOCl_4}$ the variation in $r_\mathrm{a}(\mathrm{M{=}O})$ (M = Os, Re, W) with change in *Z* is small [$r_\mathrm{a}(\mathrm{W{=}O}) - r_\mathrm{a}(\mathrm{Os{=}O}) = 0.024\ (19)$ Å] and in view of the errors is probably not significant (see Table I). However, there are significant changes in $r_\mathrm{a}(\mathrm{M{-}Cl})$ (M = W, Re, Os) with the values being in the order $r_\mathrm{a}(\mathrm{W{-}Cl}) > r_\mathrm{a}(\mathrm{Re{-}Cl}) > r_\mathrm{a}(\mathrm{Os{-}Cl})$ [$r_\mathrm{a}(\mathrm{W{-}Cl}) - r_\mathrm{a}(\mathrm{Os{-}Cl}) = 0.022\ (7)$ Å] while $r_\mathrm{a}(\mathrm{W{-}Cl})$ is equivalent to $r_\mathrm{a}(\mathrm{Mo{-}Cl})$. The results show that the effect of increases in *Z* across a period is to cause decreases in $r_\mathrm{a}(\mathrm{M{-}Cl})$. In contrast the $r_\mathrm{a}(\mathrm{M{-}Cl})$ values for the 4d and 5d members of a given group appear to be constant, the latter observation being attributable to the "lanthanide contraction" reducing bond lengths for 5d species.

That the O=W—Cl angle in $\mathrm{WOCl_4}$ is above 90° is a consequence of the influence of the electrons in the π component of the W=O bond. Indeed in $\mathrm{XeOF_4}$[5] the O=Xe—F angle is greater than 90°, thus showing that interaction between the multiple bond and the cis fluorine atoms is greater than that of the fluorine atoms with the lone pair which is trans to Xe=O. The O=M—Cl angle is larger in the osmium compound than in the related tungsten species [$\angle$O=Os—Cl - $\angle$O=W—Cl = 5.8 (1.4)°] with an accompanying decrease in the cis and trans Cl···Cl distances of 0.113 (17) and 0.159 (24) Å, respectively. The increase in $\angle$O=M—Cl along the series tungsten, rhenium, and osmium we do not believe is caused by an increase in steric requirements of the M=O double bond but is attributable to the steric influence of the presence of one electron in $\mathrm{ReOCl_4}$, and two electrons in $\mathrm{OsOCl_4}$, in the nonbonding d_{xy} orbital.

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Registry No. $\mathrm{OsOCl_4}$, 36509-15-6.

Supplementary Material Available: Tables of total scattered intensities $s^4I_\mathrm{t}(s)$ from each plate and calculated backgrounds for each plate (6 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes of a Binucleating Clathrochelate Ligand: A Reinvestigation of the Crystal Structure

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The crystal structure of the complex $\mathrm{(LFeCo)BF_4}$, where L is the ligand resulting from the condensation of 3 mol of 2-hydroxy-5-methylisophthalaldehyde and 2 mol of tris(aminoethyl)amine, has been rerefined in the rhombohedral space group $R\bar{3}c$: $a = 11.833$ Å, $c = 49.603$ Å, $Z = 6$. The two metal sites in the complex are structurally equivalent; the original refinement in space group *Cc* did not reveal this equivalence.

Recently, Timken, Marritt, Hendrickson, Gagnē, and Sinn (ref 1; hereinafter, TMHGS) reported the synthesis and magnetic properties of a number of binuclear metal complexes $\mathrm{(LM_1M_2)BF_4}$, where $\mathrm{M_1}$ and $\mathrm{M_2}$ are transition metals Cu, Fe, Co, or Mn and L is the chelating ligand resulting from the Schiff-base condensation of 3 mol of 2-hydroxy-5-methylisophthalaldehyde and 2 mol of tris(aminoethyl)amine; both homobinuclear ($\mathrm{M_1 = M_2}$) and heterobinuclear compounds were made. The structure of these compounds was characterized by a single-crystal X-ray diffraction analysis of the heterobinuclear Fe–Co compound; X-ray powder diffraction photographs indicated that all the compounds prepared, with the exception of a hydrated Cu–Cu species, are isostructural. The crystal structure of the prototypical Fe–Co compound was described as monoclinic, space group *Cc*, with the metal atoms occupying ordered, crystallographically distinct sites. On the other hand, Mössbauer measurements suggested that there is only "one type of coordination site" in the Fe–Mn complex.

We have reexamined the crystallographic data of THMGS and find that the structure of the Fe–Co compound is properly described in the rhombohedral space group $R\bar{3}c$ (No. 167) and that the two metal sites are equivalent.

Experimental Section

The monoclinic unit cell chosen by TMHGS has the dimensions $a = 20.501\ (10)$ Å, $b = 11.833\ (3)$ Å, $c = 17.889\ (9)$ Å, $\beta = 112.44\ (4)°$ and

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Table I. Atomic Parameters (Space Group $R\bar{3}c$)

		averaged from *Cc*			refined			
atom[a]	M[b]	x	y	z	x	y	z	10^3U_{eq}
FeCo	12	0	0	0.2190	0	0	0.21894 (4)	59 (1)
F1	6	0	0	0.4726	0	0	0.4714 (3)	132 (5)
F234	18	0.0190	0.1154	0.5068	0.0285 (26)	0.1196 (13)	0.5071 (3)	145 (5)
O*ABC*	18	0.1240	x	$^1/_4$	0.1216 (11)	x	$^1/_4$	91 (2)
N1	12	0	0	0.1573	0	0	0.1572 (2)	71 (2)
N3,12	36	0.0721	0.1902	0.1996	0.0720 (5)	0.1887 (5)	0.1998 (1)	60 (1)
C1,14	36	0.0300	0.1286	0.1519	0.0333 (7)	0.1310 (7)	0.1519 (1)	79 (2)
C2,13	36	0.0031	0.1949	0.1752	0.0039 (7)	0.1939 (7)	0.1754 (1)	71 (2)
C4,11	36	0.1749	0.2974	0.2059	0.1751 (7)	0.2966 (6)	0.2059 (1)	55 (2)
C5,9	36	0.2619	0.3201	0.2286	0.2621 (6)	0.3208 (6)	0.2285 (1)	50 (2)
C6,8	36	0.3789	0.4371	0.2295	0.3785 (7)	0.4379 (7)	0.2293 (1)	62 (2)
C7	18	0.4747	x	$^1/_4$	0.4712 (15)	x	$^1/_4$	74 (3)
C10	18	0.2306	x	$^1/_4$	0.2298 (15)	x	$^1/_4$	53 (2)
CM	18	0.5972	x	$^1/_4$	0.5949 (21)	x	$^1/_4$	125 (4)
B	6	0	0	$^1/_2$	0	0	$^1/_2$	54 (4)

[a] The numbering system combines the numbers of the atoms from TMHGS that were averaged. [b] Site multiplicity. [c] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i^*a_j^*)(\vec{a}_i\cdot\vec{a}_j)]$.

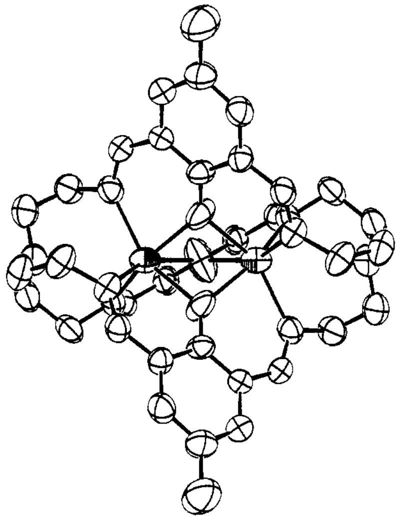

Figure 1. Projection of the cation, viewed down one of the 2-fold axes.[4] The 3-fold axis passes horizontally through the two iron atoms (shown with octant shading). Thermal ellipsoids are shown at the 50% probability level.

$Z = 4$. The vectors $(0\bar{1}0)$, $(^1/_2{}^1/_20)$, and (103) describe a rhombohedral cell with (hexagonal) dimensions $a = 11.833$ Å, $b = 11.835$ Å, $c = 49.603$ Å, $\alpha = 89.99°$, $\beta = 90.00°$, $\gamma = 119.99°$, and $Z = 6$. The atom coordinates published by TMHGS, first translated to $x' = x + 0.219$, $y' = y - 0.250$, $z' = z + 0.407$ (to move the origin to the conventional one in $R\bar{3}c$) and then transformed by the matrix $(1,-1,-^1/_3)$, $(2,0,-^2/_3)$, $(0,0,^1/_3)$, conform quite closely to the symmetry requirements of space group $R\bar{3}c$; suitable averaging led to our starting parameters (Table I). The F values deposited by TMHGS (their supplementary material) represented 2027 reflections with $F_0^2 \geq 3\sigma(F_0^2)$; when we averaged them according to Laue symmetry $\bar{3}m$ the R factor for averaging was 0.06, and 815 independent reflections resulted. Full-matrix refinement in $R\bar{3}c$, with half-iron and half-cobalt atoms in the metal sites, converged at an R ($\sum|F_o - |F_c||/\sum F_o$) of 0.074; the hydrogen atoms were included at calculated positions (C–H = 0.98 Å) with isotropic B's of 5.0 Å^2, and the remaining atoms were given anisotropic U_{ij}'s. The distribution parameter of the Fe–Co site was then allowed to vary from 0.5; it converged at the value 1.4 (1) as the proportion of Fe in the site (and, accordingly, –0.4 Co!). The site was therefore presumed to be fully occupied by Fe, and final convergence was reached at an R of 0.072 for 815 reflections and 95 parameters. While this value is a bit high, it compares favorably with the R of 0.083 reported by TMHGS for 2027 (unaveraged) reflections and 410 parameters; TMHGS noted that the crystal had "poor diffraction quality".

Discussion

The most important result of this reinvestigation is the finding that the two metal sites are structurally equivalent. The symmetry of the binuclear complex (see Figure 1) is 32 (D_3), and the metal atoms lie on 3-fold axes; thus, all six M–N distances in the complex are equal, at 2.170 (6) Å, as are the six M–O distances, at 2.109 (13) Å; in the earlier *Cc* description the M–N distances ranged from 2.09 (1) to 2.26 (1) Å and M–O from 2.04 (1) to 2.20 (1) Å. Bond distances and angles in the ligand are normal. The BF_4^- group lies on a site of $\bar{3}$ symmetry, with the F atoms disordered.

It is possible that the crystal chosen for X-ray measurements by TMHGS was the homobinuclear Fe–Fe compound rather than the heterobinuclear Fe–Co, although the method of preparation makes this unlikely. Possibly a few such crystals formed during the synthesis of the heterobinuclear material, and one of these crystals happened to be selected. In view of the powder-diffraction fingerprinting carried out by TMHGS, the crystal structure of the heterobinuclear Fe–Co species would be expected to be almost identical with what we report here, with the Fe and Co atoms randomly distributed between the two equivalent metal sites. The Mössbauer studies of TMHGS support this model.

The change in space group from *Cc* to $R\bar{3}c$ involves both a change in the lattice type and the addition of an inversion center. The correct lattice type (and, hence, Laue symmetry), which requires the cation to have 3-fold symmetry, should have been suggested by a systematic check of the reduced cell and its Niggli matrix.[2] The center of symmetry, which requires that the two metal sites be equivalent, should have been evidenced by near singularities in the least-squares matrix;[3] indeed, TMHGS noted that interchanging the Fe and Co atoms in their *Cc* model led to "unusually large thermal parameters for the metal atoms"—a surprising result that might have suggested the near centrosymmetry of their model. We continue to urge extreme care in choosing the most appropriate unit cell and space group.

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Registry No. (LFeCo)BF_4, 98943-54-5.

Supplementary Material Available: Tables of anisotropic U_{ij}'s, coordinates assigned to the H atoms, and selected bond lengths and angles (3 pages); a table of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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