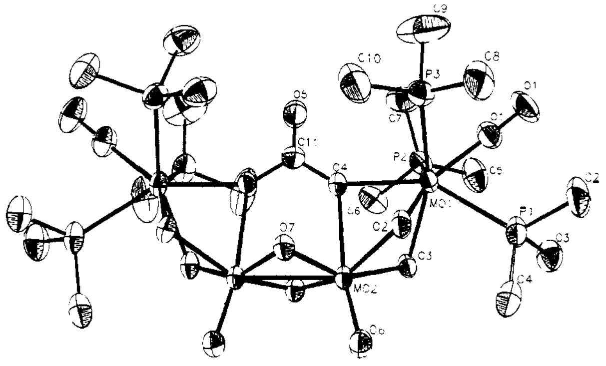
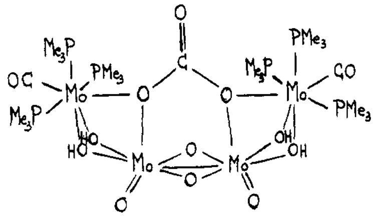


Figure 1. Molecular structure of the carbonate complex **4** [$Mo_4(\mu_4$-$CO_3)(CO)_2(O)_2(\mu_2$-$O)_2(\mu_2$-$OH)_4(PMe_3)_6$].

If *cis*-[$Mo(N_2)_2(PMe_3)_4$] and CO_2 are reacted at room temperature and pressure, in a 2:1 acetone:toluene mixture, complex **2** crystallizes upon standing for a period of 1–3 days. If the mixture is allowed to stand at 20–25 °C for 15–20 days, small amounts of red-orange crystals[9] of a complex characterized by X-ray crystallography as an unusual mixed-valence Mo^{II}–Mo^{V} species of composition [$Mo_4(\mu_4$-$CO_3)(CO)_2(O)_2(\mu_2$-$O)_2(\mu_2$-$OH)_4(PMe_3)_6$] (**4**) are also obtained. Complex **4** contains a bidentate, quadruply bridging CO_3 group, engaged in a novel mode of binding. The molecular structure and atom labeling scheme for **4** are presented in Figure 1.[10] The molecule resides on a crystallographic 2-fold axis that contains C11 and O5 of the carbonate ligand. The carbonate ligand bridges all four molybdenum atoms, with two molybdenum atoms bonded to each carbonate oxygen off the symmetry axis (Mo1–O4 = 2.221 (3) Å, Mo2–O4 = 2.419 (4) Å). The outer Mo^{II} atoms are seven coordinate, bonded to one oxygen of the carbonate ligand, two bridging hydroxy ligands, three trimethylphosphine groups, and a carbonyl moiety. The overall coordination about these Mo^{II} atoms is similar to that found for [$Mo(\mu$-$CO_3)(CO)(PMe_3)_3]_2$[7] (**3**) and [$Mo(\mu$-$CO_3)(CO)(PMe_2Ph)_3]_2$.[2]



4

The two inner Mo^{V} atoms show bonding characteristics similar to other $Mo_2O_4^{2+}$ moieties that have been structurally characterized;[11] these include a Mo–Mo single bond (2.5522 (9) Å), a bent bridging arrangement of oxygen atoms to form a distorted octahedral coordination about the Mo^{V} atoms, and a terminal oxo group (Mo2–O6 = 1.672 (4) Å) that weakens the bond trans to it (Mo2–O4 = 2.419 (4) Å). Although it is not easy to rationalize the formation of this complex, it is evident that small amounts of water present in the acetone used must play an important role. Data available so far suggest the implication of **3** at some stages of the reaction.

Acknowledgment. We are grateful to the Spanish CAICYT (E.C.) and Ministerio de Educación y Ciencia (J.M.M. and M.L.P.) and to the U.S. National Science Foundation (J.L.A.) for support of this work.

Registry No. 1, 85405-72-7; **2**, 85405-73-8; **3**, 85405-74-9; **4**, 85405-75-0; *cis*-[$Mo(N_2)_2(PMe_3)_4$], 82044-78-8; CO_2, 124-38-9.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors for **4** (13 pages). Ordering information is given on any current masthead page.

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(9) **4**: IR (Nujol) 3570, 3400 (OH), 1760 (CO), 1560, 1280, 1080 (CO_3^{2-}), 975 (Mo=O), and 945 cm; (PMe_3). Anal. Calcd for $Mo_4C_{21}H_{58}O_{13}P_6$: C, 23.17; H, 5.33; O, 19.1. Found: C, 24.32; H, 5.63; O, 18.7. In addition to **2** and **4**, *cis*-[$Mo(CO)_2(PMe_3)_4$] was crystallized from the mother liquor.

(10) **4** crystallizes in the orthorrhombic space group *Pbcn* with lattice constants a = 26.866 (9) Å, b = 12.934 (4) Å, c = 11.965 (2) Å, and D_{calc} = 1.74 g cm^{-3} for four tetrametallic units in the cell. Least-squares refinement based on 1638 observed reflections led to a final R value of 0.018.

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Anion Ordering in Mixed-Valence Cs_2SbCl_6 and Related Salts

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Cs_2SbCl_6, first prepared in 1901,[1] was originally described as an Sb^{IV} salt. However, a great deal of spectroscopic evidence (e.g., Mössbauer,[2] far infrared,[3] Raman,[4] ultraviolet,[5] and photoelectron spectra[6]) points to the existence of distinguishable $Sb^{III}Cl_6^{3-}$ and $Sb^{V}Cl_6^{-}$ in the structure, and its semiconductivity[7] and visible absorption[5,8] show that Cs_2SbCl_6 is a classical Robin–Day[9] class II mixed-valency compound. Additional recent measurements[10] of the far infrared and Raman spectra have also been interpreted in terms of increased localization of the Sb oxidation states at low temperature. Nevertheless, there remains a puzzle about its crystal structure. Wells[1] showed that Cs_2SbCl_6 forms mixed crystals with salts like Cs_2SnCl_6 and Cs_2PtCl_6, and early X-ray powder diffraction patterns[11,12] were indexed by using the space group *Fm*3*m*. X-ray powder photographs of mixed-metal compounds $Cs_2M^{III}{}_{0.5}Sb_{V0.5}Cl_6$[8] were also indexed as *Fm*3*m*, implying that the MCl_6^{3-} and $SbCl_6^{-}$ groups were randomly distributed. Given the difference in charge between the two anions, this seems inherently unlikely, and given that the X-ray scattering is dominated by the Cs and Sb, we have recorded neutron powder diffraction profiles of Cs_2SbCl_6 itself and a number of mixed-metal analogues. We find that there is indeed a superlattice ordering of Sb^{III} (and other M^{III}) and Sb^{V} at low temperature in several salts of this type, while others remain disordered. The presence or absence

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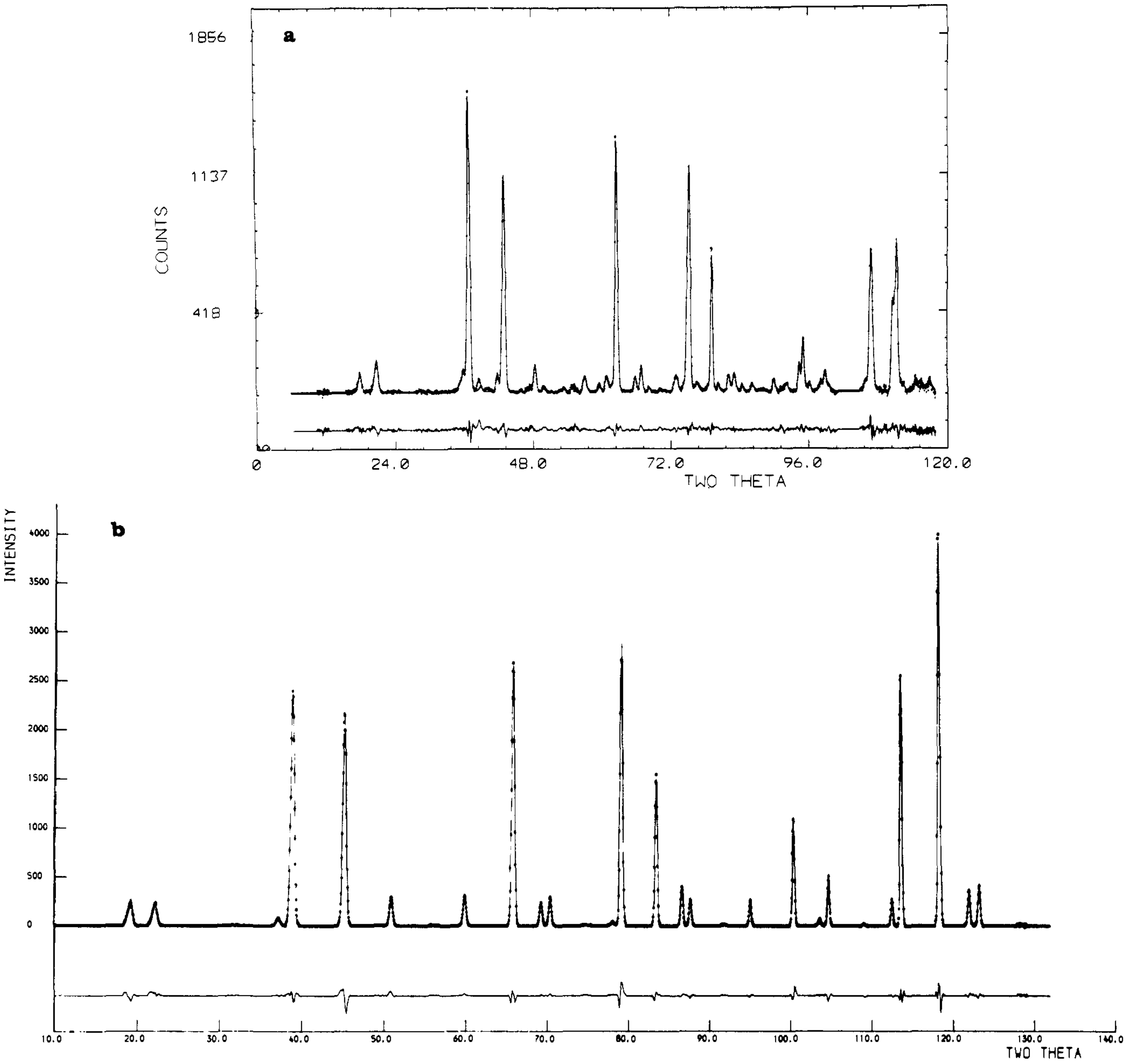

Figure 1. Powder neutron diffraction profiles of (a) $Cs_2Sb_{0.5}{}^{III}Sb_{0.5}{}^{V}Cl_6$ and (b) $Rb_2Fe_{0.5}{}^{III}Sb_{0.5}{}^{V}Cl_6$.

Table I. Unit Cell Parameters and Bond Lengths for $A_2M^{III}{}_{0.5}Cl_6$ (Å)

A	M^{III}	a_0	c_0	av M^{III}-Cl	av Sb^V-Cl	$M^{III,V}$-Cl	R_{wpr}, %^{a}
Cs	Bi	10.3558 (2)	20.8415 (6)	2.683	2.398	2.541	9.15
	Sb	10.3092 (3)	20.7288 (7)	2.646	2.384	2.515	9.20^b
	Tl	10.2994 (4)	20.6114 (15)	2.554	2.389	2.472	11.40
	In	10.2788 (2)				2.438	11.78
	Fe	10.2044 (1)				2.386	8.29
Rb	Tl	10.0613 (1)				2.448	9.26
	In	10.0307 (1)				2.426	7.33
	Fe	9.9437 (1)				2.379	8.40
	Rh	9.9093 (1)				2.361	8.66

[a] *R* defined in ref 16. [b] Biphasic refinement.[15]

of superlattice ordering correlates with the average $M^{III,V}$–Cl bond length.

The powder neutron diffraction profiles were recorded at 4.7 K on the D1A diffractometer at the Institut Laue-Langevin, Grenoble. The samples were contained in vanadium cans held in a helium cryostat, and the mean neutron wavelength was 1.909 Å. All the compounds were prepared by standard methods[1,8] and had been carefully checked by X-ray powder diffraction to ensure that they were free of trace impurities of starting materials. A small amount of α-$Cs_3Sb_2Cl_9$ was identified as an impurity in Cs_2SbCl_6 (see below). Typical scans of Cs and Rb salts are shown in Figure 1. The background has been subtracted. It is clear at once that, in addition to the major reflections common to both compounds, the Cs salt (Figure 1a) has numerous weaker reflections indicative of superlattice ordering. All the reflections observed in $Rb_2Fe_{0.5}Sb_{0.5}Cl_6$ (Figure 1b) are accounted for by the space group $Fm3m$ with $a_0 = 9.944$ Å, and all the "extra" reflections in the Cs profile (Figure 1a) are described by the tetragonal space group $I4_1/amd$ with $a_0 = 10.309$ Å and $c_0 = 20.729$ Å. Refinement of each profile by the Rietveld technique[13] using the POWDER system[14] on the SERC Interactive Computing Facility leads to the fits shown in Figure 1 and the unit cell parameters and bond lengths listed in Table I. In refining the Cs_2SbCl_6 profile, account was taken of the $Cs_3Sb_2Cl_9$ impurity by using a multiphase fitting procedure.[15] An absorption correction was applied to all the powder diffraction profiles by Hewat's method.[16]

The proposed ordering of $M^{III}Cl_6^{3-}$ and $Sb^VCl_6^-$ in the tetragonal salts is similar to that postulated in a single-crystal X-ray diffraction study of $(NH_4)_2SbBr_6$.[17] Each $M^{III}Cl_6^{3-}$ is surrounded by eight $SbCl_6^-$ and four $M^{III}Cl_6^{3-}$, the latter at the corners of a tetrahedron. The $Fm3m$ unit cell (that of the K_2PtCl_6 structure) is doubled along one axis. In contrast to $(NH_4)_2SbBr_6$[17] we find less than 0.5° angular distortion of the $SbCl_6^-$ but a small (2.5°) D_{2d} distortion of $SbCl_6^{3-}$ and $BiCl_6^{3-}$, to be compared with $TlCl_6^{3-}$, which showed an angular distortion of 1.5°. In the cubic salts the space group constrains all anions to be octahedral. An important parameter in theories of electron transfer in mixed-valency compounds is the difference in bond lengths around the ions of different oxidation state. In the present case we find Sb^{III}–Cl is 2.646 and Sb^V–Cl 2.384 Å compared with 2.63 and 2.35 Å in $(C_3H_7NH_3)_4Sb_{0.5}{}^{III}Sb_{0.5}{}^VCl_6(Cl)_2$,[16] which has a rather different structure. Of the nine salts $A_2M_{0.5}{}^{III}Sb_{0.5}{}^VCl_6$ investigated, three were found to have superlattice ordering of $M^{III}Cl_6^{3-}$ and $Sb^VCl_6^-$, the rest being disordered. All the Rb salts were disordered, and among the Cs salts ordering was found in both salts in which M^{III} had an ns^2 electron configuration and one where M^{III} was an ns^0 ion (Tl^{III}). To identify the reasons for this result, we note that the average (M^{III},Sb^V)–Cl bond lengths span a range from 2.541 to 2.361 Å (Table I). The change from order to disorder occurs between 2.472 ($Cs_2Tl_{0.5}Sb_{0.5}Cl_6$) and 2.448 Å ($Rb_2Tl_{0.5}Sb_{0.5}Cl_6$). Salts with an average (M^{III},Sb^V)–Cl bond length greater than 2.472 Å are ordered while all those where it is less than 2.448 Å are disordered. Thus the difference in size between MCl_6^{3-} and $SbCl_6^-$ appears to be the dominant factor. Unfortunately $Rb_2Sb_{0.5}{}^{III}Sb_{0.5}{}^VCl_6$ is very unstable and transforms easily to the monoclinic salt $Rb_{2.67}SbCl_6$, but we are continuing powder neutron diffraction work on the hexabromoantimonates(III,V) and related mixed-metal salts to clarify the structural principles governing this class of compound.

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Registry No. $Cs_2Bi^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 12441-33-7; $Cs_2Sb^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 17805-64-0; $Cs_2Tl^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 41875-61-0; $Cs_2In^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 41875-60-9; $Cs_2Fe^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 61269-02-1; $Rb_2Tl^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 12432-76-7; $Rb_2In^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 85370-04-3; $Rb_2Fe^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 61269-01-0; $Rb_2Rh^{III}{}_{0.5}Sb^V{}_{0.5}Cl_6$, 85370-05-4.

Supplementary Material Available: Table of positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Syntheses and Structures of Anionic *closo*-Rhodacarborane Clusters That Contain a Formal Rhodium(I) Vertex

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Structural characterization of electron-rich metallacarboranes has been of interest since the earliest crystallographic studies showed that some late transition-metal metallacarboranes adopt significantly distorted polyhedral structures.[1] The importance of the electronic configuration of the metal was immediately recognized,[2] but more recent structural studies of 12-vertex platinum and palladium metallacarboranes have shown that the degree of polyhedral distortion is also a sensitive function of the ancillary ligands, the relative positions of the carbon atoms present in the carborane ligand and the metal itself.[3] Prompted by these unique structural findings, Mingos has completed extended Hückel calculations on model icosahedral platinacarboranes and has explained the conformations and polyhedral distortions adopted by late transition-metal metallacarboranes.[3e,4] While there are many examples of icosahedral d^8 L_2M^{II} (L = CO, RNC, PR_3; M = Ni,[5] Pd,[3] Pt[3]) metallacarboranes, isolation of isoelectronic L_2M^I (M = Co, Rh, Ir) metallacarboranes has proven to be more elusive. Only one example of the latter, namely, 3-(Ph_3P)-3-CO-4-(C_5H_5N)-3,1,2-$RhC_2B_9H_{11}$, has been structurally characterized,[6] and the conformation of the metal vertex proved to be incompatible with molecular orbital predictions. Thus, in order to evaluate structural consequences of icosahedral d^8 rhodium(I) metallacarboranes, we have synthesized and structurally characterized salts of $[3,3\text{-}(Ph_3P)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$ and $[2,2\text{-}(Ph_3P)_2\text{-}2,1,7\text{-}RhC_2B_9H_{11}]^-$. Structures of these two anions provide the first opportunity to evaluate the effects of introducing identical d^8 metal centers into isomeric 7,8- and 7,9-$C_2B_9H_{11}^{2-}$ ligands. Furthermore, we are not aware of any other structurally characterized monometallic anions that contain both formal Rh(I) and PPh_3 ligands.

Isomeric hydridorhodacarborane clusters 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$[7a] (**1a**), 2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$[7a] (**1a**), 2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$[7a] (**1b**), and 2,2-$(Ph_3P)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$[7b] (**1c**) react with many bases (e.g., KOH, NaH, K-Selectride) at the rhodium vertex to generate air-sensitive anionic rhodacarboranes **2a–c**, respectively. On the basis of analytical and spectroscopic data,[8] each of these anions was formulated as $[(Ph_3P)_2RhC_2B_9H_{11}]^-$, available (85% yield) as crystalline tetraalkylammonium salts or potassium 18-crown-6 salts. Ethanol suspensions of complexes **2a–c** reacted with dilute

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