Registry No. $TeF_5N{=}CCl_2$, 87191-36-4; $TeF_5N{=}C(Cl)CF_3$, 87191-37-5; TeF_5NHCF_3, 87206-80-2; $Cs^+[N(CF_3)TeF_5]^-$, 98720-66-2; $Hg[N(CF_3)TeF_5]_2$, 98720-67-3; $TeF_5N{=}CF_2$, 98720-68-4; $TeF_5N{=}C(F)N(CF_3)TeF_5$, 98720-69-5; $TeF_5NHC(F){=}NCF_3$, 98720-70-8; $TeF_5N(F)CF_3$, 98720-71-9; $TeF_5N(Cl)CF_3$, 87191-40-0; $TeF_5N(Br)CF_3$, 87191-41-1; $TeF_5N(I)CF_3$, 98720-72-0; $TeF_5N(CF_3)C(O)CH_3$, 98720-73-1; $(TeF_5)_2NCF_3$, 87191-42-2; $TeF_5N(SF_5)CF_3$, 98720-74-2; $TeF_5N(CF_3)CH_2CH_2Br$, 98720-75-3; $TeF_5N{=}C(Cl)OCH_3$, 98720-76-4; $TeF_5N{=}C(OCH_3)_2$, 98720-77-5; $TeF_5N{=}C{=}NCF_3$, 98720-78-6; $K^+[TeF_5NC(F)NCF_3]^-$, 98735-50-3; $TeF_5N(CF_3)CF_2CF(CF_3)Br$, 98720-79-7; $TeF_5N(CF_3)CF(CF_3)CF_2Br$, 98720-80-0; TeF_5Cl, 21975-44-0; HgF_2, 7783-39-3; ClCN, 506-77-4; CF_3CN, 353-85-5; HF, 7664-39-3; CsF, 13400-13-0; $(CH_3)_3SiCl$, 75-77-4; KF, 7789-23-3; F_2, 7782-41-4; ClF, 7790-89-8; Cl_2, 7782-50-5; Br_2, 7726-95-6; BrF, 13863-59-7; ICl, 7790-99-0; CH_3COBr, 506-96-7; SF_5Cl, 13780-57-9; CO, 630-08-0; C_2H_2, 74-86-2; C_2H_4, 74-85-1; C_3F_6, 116-15-4.

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Dimagnesium Cobalt(I) Pentahydride, Mg_2CoH_5, Containing Square-Pyramidal CoH_5^{4-} Anions

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Mg_2CoH_5 and its deuteride have been prepared as black crystalline solids by a sintering technique at temperatures between 620 and 770 K and hydrogen (deuterium) pressures between 40 and 60 bar. X-ray and neutron powder diffraction data recorded at room temperature suggest a tetragonally distorted CaF_2-type metal atom structure (for the deuteride $a = 4.463$ (4) Å, $c = 6.593$ (6) Å, space group $P4/nmm$, and $Z = 2$). The D atoms surround the Co atoms in an ordered square-pyramidal configuration (d[Co–D] = 1.590 (17) Å (apical) and 1.515 (3) Å (basal)). The structure transforms at 488 (5) K into a disordered cubic modification ($a = 6.453$ (6) Å, at 498 K). The heat of dissociation of the hydride as measured from pressure–composition isotherms is 86 (5) kJ/mol of H_2. The electrical resistivity suggests nonmetallic behavior.

Introduction

During a search for new hydrogen storage materials that contain 3d transition-metal elements, we have recently discovered a ternary metal hydride of composition Mg_2FeH_6 in which the iron atoms were surrounded octahedrally by hydrogen atoms.[1] In this paper we report the synthesis, structure, and properties of a ternary metal hydride of composition Mg_2CoH_5 in which the cobalt atoms are surrounded by hydrogen atoms in a square-pyramidal configuration. The compound is structurally related to, but not isostructural with, the reported tetragonal low-temperature modification of Sr_2IrD_5.[2] It can be considered as an intermediate member in the isoelectronic structural series Mg_2NiH_4–Mg_2CoH_5–Mg_2FeH_6. A preliminary account of the results presented in this article has appeared elsewhere.[3]

Experimental Section

Synthesis. The hydride was prepared according to the sintering technique described previously.[1] Magnesium powder (Ventron, 50 mesh, M2N8) and cobalt powder (Puratronic, 99.998% purity) were mixed in a 2:1 atomic ratio of Mg:Co, pressed under 6 kbar to cylindrical pellets, placed in a steel autoclave, and treated for several days at temperatures between 690 and 720 K and hydrogen pressures between 40 and 60 bar. The synthesis of the deuteride was identical with that of the hydride except that it required a lower sintering temperature (670–700 K).

Purification. Under the above experimental conditions the reaction

$$4Mg + 2Co + 5H_2 \rightarrow 2Mg_2CoH_5$$

did not proceed to completion (see Results). The unreacted phases (mainly MgH_2 and Co metal) were removed as follows. The powders were suspended in chloroform and magnetically stirred. The free cobalt adhered to the magnetic stirrer and was removed mechanically. The products were then dried and suspended in purified 1,2-dibromoethane (density 2.15 g/cm^3) such that MgH_2 (density 1.42 g/cm^3) floated to the surface of the tube and could be removed. The remaining black powders were dried and analyzed. They were stable in air over a period of several weeks.

Structure Analysis. The structure analysis was performed by X-ray powder diffraction methods (Guinier photographs) at room temperature (Co Kα_1 radiation, $\lambda = 1.7889$ Å) and in the temperature range between 300 and 550 K (Cu Kα_1 radiation, $\lambda = 1.5405$ Å), and by neutron powder diffraction at 498, 298, and 9 K (powder diffractometer DMC, equipped with a multidetector at the reactor SAPHIR at Würenlingen,[4] $\lambda = 1.184$ (1) Å, $[(\sin\theta)/\lambda]_{max} = 0.77$ Å^{-1}; scattering lengths used (10^{-12} cm) were 0.538 (Mg), 0.253 (Co) and 0.667 (D)). A purified sample (ca. 3 cm^3) was placed in a cylindrical vanadium container of 10 mm diameter. The structure refinement was performed by the Rietveld profile fitting method,[5] using the neutron diffraction data recorded at 298 K, and a computer program written,[6] for the simultaneous treatment of two phases.

Pressure–Composition Isotherms. The thermal stability of Mg_2CoH_5 was determined from pressure–composition isotherms as measured on unpurified samples in the temperature range between 620 and 720 K. The experimental setup was identical with that described in ref 7.

Magnetization Measurements. The magnetic susceptibility of the purified deuteride sample was measured as a function of an applied magnetic field (up to 80 kG) and temperature (60–300 K) by using a SQUID magnetometer described in ref 8.

Electrical Resistivity. The electrical resistivity was measured as a function of temperature (4–24 K, 300 K) using the four-point method. For this purpose two purified hydride samples were pressed under 10 kbar pressure into cylindrical pellets and cut into slabs of about 5-mm length and 1–1.5-mm width.

Results

The Mg–Co mixtures that were sintered in hydrogen (deuterium) atmosphere showed a weight increase of up to 3.5% (7%). The reaction products consisted of fine black powders, which contained small concentrations of white particles (MgH_2). X-ray analysis confirmed the formation of a new ternary hydride (deuteride) phase and revealed the presence of about 25% impurity phases (mainly MgH_2 or MgD_2, and elemental Co). After purification the fraction of impurity phases was reduced to less than 8% (estimated from neutron data and magnetization measurements). An attempt was made to measure the compositional ratio Mg:Co by X-ray fluorescence analysis as well as by atomic absorption. Although the results were consistent with the expected

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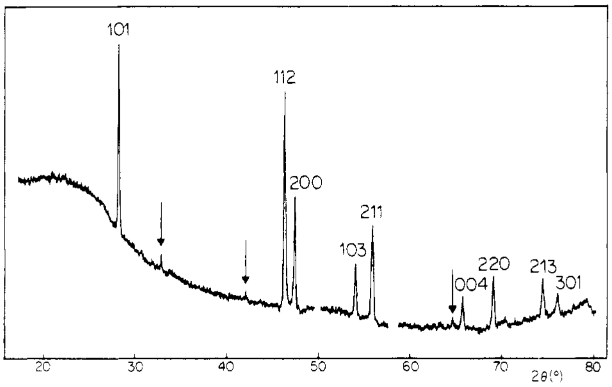

Figure 1. X-ray powder diffraction pattern of tetragonal Mg_2CoD_5 at room temperature (Co $K\alpha_1$ radiation, $\lambda = 1.7889$ Å). The main MgD_2 peaks are marked by arrows, and two camera lines are omitted.

Table I. Structural Data for Mg_2CoD_5 ($T = 298$ K)[a]

space group $P4/nmm$ (No. 129, origin at center)
cell params, Å $a = 4.463$ (4), $c = 6.593$ (6), $c/a = 1.4774$ (2)

Positional and Isotropic Thermal Parameters

		x	z	B, Å^2	B, Å^2
Mg(1)	2a	$^3/_4$	$^1/_4$	0	0.04 (4)
Mg(2)	2b	$^3/_4$	$^1/_4$	$^1/_2$	0.04 (-)[b]
Co	2c	$^1/_4$	$^1/_4$	0.2561 (20)	0.35 (15)
D(1)	2c	$^1/_4$	$^1/_4$	0.4972 (17)	1.44 (9)
D(2)	8j	0.4879 (4)	0.4879 (-)	0.2257 (3)	1.39 (5)

R Factors

$R_{wp} = 0.12$, $R_{exp} = 0.05$, $R_F = 0.08$ for 178 Mg_2CoD_5 reflections

[a] Figures in parentheses are esd's calculated by the Rietveld program,[6] except for the esd's of the cell constants (estimated from the uncertainty of λ). [b] Value constrained.

ratio of 2 (atomic absorption 2.22 (20), X-ray fluorescence 1.74 (18)), they did not allow us to make an estimation of the amounts of impurity phases present in the samples. In samples that were sintered at temperatures above 720 K another ternary hydride phase was found, which, however, was not further investigated.

The X-ray and neutron powder diffraction patterns of the purified deuteride sample are shown in Figures 1 and 2, respectively. In the X-ray pattern all reflections were indexed on a tetragonal cell with $a = 4.471$ (3) Å and $c = 6.605$ (4) Å; $c/a = 1.477$ (hydride $a = 4.480$ (2) Å and $c = 6.619$ (3) Å; $c/a = 1.477$). Patterns of other (nonpurified) samples that were prepared under slightly different experimental conditions yielded cell parameters which did not differ significantly from those given above. The absence of strong reflections, *hkl*, satisfying the condition $h + k + l =$ odd, suggested that the Bravais lattice of the metal atom substructure was nearly body centered (for overall symmetry of the structure see below). The reflection intensities were consistent with the assumption of a tetragonal distorted CaF_2-type metal atom arrangement ($c/a = 1.477$, $c \sim a_{cub}$, $a \sim a_{cub}/2^{1/2}$) similar to that reported for the body-centered tetragonal low-temperature phase of Sr_2IrD_5[3] ($c/a = 1.465$, proposed space group $I4/mmm$; Sr in 4d (0, $^1/_2$, $^1/_4$) etc., Ir in 2a (0, 0, 0), etc.). However, in contrast to the latter deuteride the overall lattice symmetry of Mg_2CoD_5 was primitive because its neutron diffraction pattern contained relatively strong reflections, *hkl*, with $h + k + l =$ odd (see, for example, the reflections 111, 201, and 223 in Figure 2b).

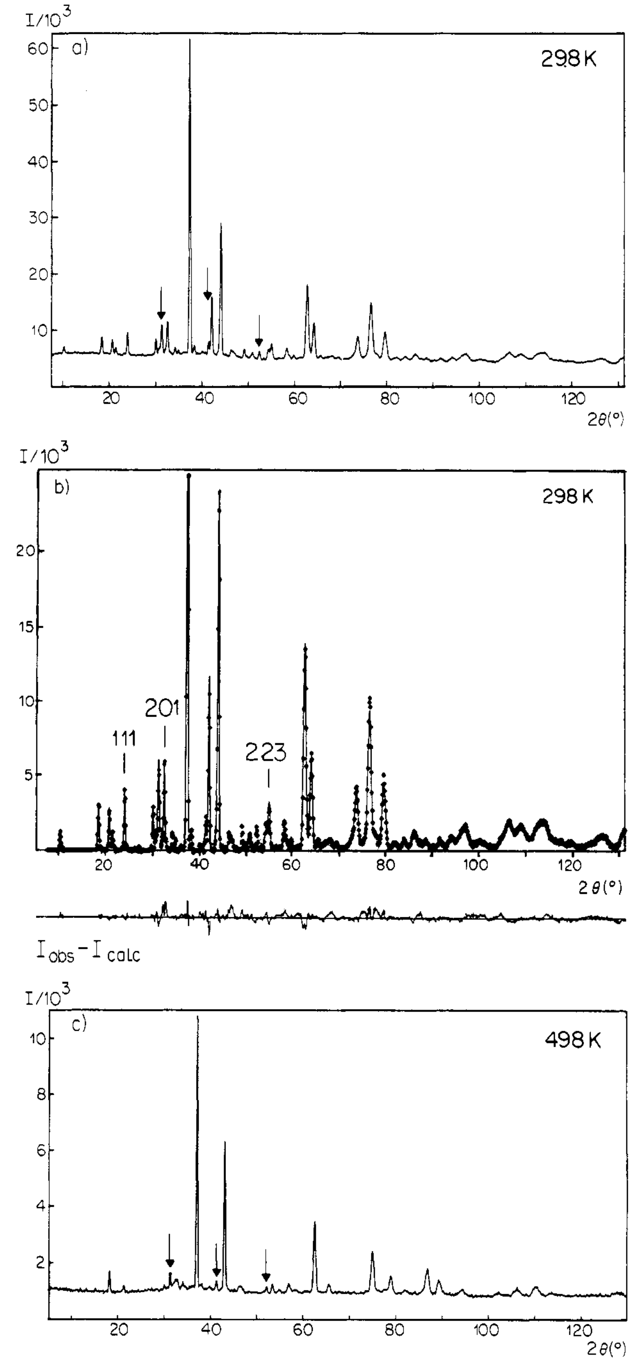

Figure 2. Neutron powder diffraction patterns ($\lambda = 1.184$ (1) Å) of Mg_2CoD_5 with impurity phase MgD_2: (a) absorption-corrected experimental pattern at 298 K; (b) experimental vs. calculated (top) and difference pattern (bottom) of the tetragonal phase at 298 K, note the labeled peaks with $hkl = 2n + 1$; (c) experimental pattern of the cubic modification at 498 K). Positions of main MgD_2 peaks are marked by arrows in parts a and c.

Good agreement between the observed and calculated intensity profiles was obtained in space group $P4/nmm$ by assuming two symmetry-independent D atoms, which surrounded the Co atoms in an ordered square-pyramidal configuration. The structure model was refined to $R_{wp} = 0.12$ on the room-temperature data by using Gaussian peak shapes. The background contribution was subtracted by hand. The following 19 parameters were allowed to vary: two scale factors, three peak width parameters, one zero correction factor, four cell parameters, and nine atomic parameters (one for MgD_2 and eight for Mg_2CoD_5). No preferred orientation parameter was refined, because no evidence for anisotropic crystallites was found. A total of 255 reflections contributed to the refinement, of which 178 belonged to Mg_2CoD_5 and 77 to MgD_2. Except for MgD_2 no peaks due to impurity phases could be detected. In particular the scattering contribution of the Co impurity (see Magnetization Measurements) is more than 1 order of magnitude smaller than that of MgD_2 and could be neglected. The results of the structure refinement of Mg_2CoD_5 are summarized in Table I. A list of bond distances is given in Table II. A comparison between the observed and calculated powder diffraction pattern is given in Figure 2b. A drawing of the main structural unit of Mg_2CoD_5 is represented in Figure 3. A final least-squares cycle was calculated in which the occupancy factors

Table II. Interatomic Distances (Å) for Tetragonal Mg_2CoD_5 ($T = 298$ K)

Co–4Mg(1)	2.798 (8)	D(1)–4Mg(2)	2.232 (2)
–4Mg(2)	2.751 (8)	–Co	1.590 (17)
–D(1)	1.590 (17)	–4D(2)	2.337 (9) (intra)
–4D(2)	1.515 (3)	–4D(2)	2.465 (9) (inter)
Mg(1)–4Co	2.798 (8)	D(2)–2Mg(1)	2.170 (2)
–8D(2)	2.170 (2)	–2Mg(2)	2.402 (2)
Mg(2)–4Co	2.751 (8)	–Co	1.515 (3)
–4D(1)	2.232 (2)	–D(1)	2.337 (9) (intra)
–8D(2)	2.402 (2)	–D(1)	2.465 (9) (inter)
		–2D(2)	2.124 (3) (intra)
		–2D(2)	2.340 (3) (inter)

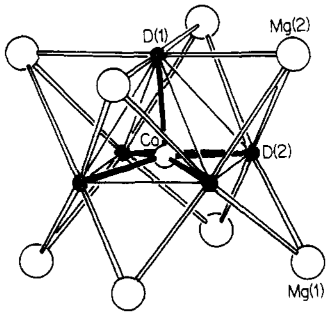

Figure 3. Structural unit of Mg_2CoD_5 at room temperature; site symmetry of Co: $4mm$.

of the two D sites were allowed to vary together with all other parameters. The values obtained (1.08 (3) for D(1) and 1.02 (2) for D(2)) indicated that a possible deuterium deficiency of the compound was small. The refinement on the low-temperature data ($R_{wp} = 0.12$) yielded atomic parameters that did not differ significantly from those obtained on the room-temperature data.

The high-temperature X-ray and neutron diffraction patterns revealed the occurrence of a structural phase transformation at 488 (5) K (upon heating) and 480 (5) K (upon cooling). It leads to a structure of cubic symmetry with cell parameter $a = 6.453$ (6) Å (at 498 K). A profile refinement based on the neutron diffraction data recorded at 498 K (Figure 2c) confirmed the CaF_2-type metal atom arrangement (space group $Fm3m$) and a disordered distribution of D atoms similar to that found in the cubic high-temperature phases of Mg_2NiD_4[9,10] and Sr_2IrD_5.[2] The refinement of the D sites yielded for the position 24e (x, 0, 0) with $x = 0.2368$ (6) an occupancy of 0.86 (2) as compared to 0.833 for a statistical distribution of five D's over six sites. As expected, the refined temperature factor of the deuterium site ($B_D = 3.1$ (2) $Å^2$) was higher than those of the metal atom sites ($B_{Co} = 0.7$ (2), $B_{Mg} = 0.9$ (2) $Å^2$) and those obtained from the room-temperature data ($\langle B_D \rangle = 1.4$ (1) $Å^2$) and the low-temperature data ($\langle B_D \rangle = 1.0$ (1) $Å^2$).

The pressure–composition isotherms of the hydride samples showed two plateaus, of which that at higher pressures was ascribed to MgH_2 and that at lower pressures to Mg_2CoH_5. The logarithmical dependency of the latter on the inverse temperature allowed us to estimate the following enthalpies of formation: 86 (5) kJ/mol of H_2 (desorption) and −60 (5) kJ/mol of H_2 (absorption).

The electrical conductivity measurements of Mg_2CoH_5 yielded resistivity values of the order of 10^8–10^9 $\mu\Omega$ cm at room temperature. The resistivity ratio $\rho(T)/\rho(298\ K)$ increased from 2.5–3.0 (at 24 K) to 7–8 (at 4.2 K). This behavior is consistent with the assumption of nonmetallic behavior.

As to the magnetic properties of Mg_2CoH_5 no definite conclusion could be drawn from the magnetization measurements because the purified samples all contained significant amounts of ferromagnetic cobalt metal. The magnetic susceptibility value, χ_g, obtained from extrapolation to high magnetic fields ($\chi_g = 3$ (2) $\times 10^{-6}$ emu/g) was consistent with the assumption of weakly paramagnetic (or possibly diamagnetic) behavior. The amount of free cobalt in the sample (2.7 wt %) was estimated from the magnetization values above saturation (10 kG).

Discussion

Dimagnesium cobalt(I) hydride, Mg_2CoH_5, is a further member of the structural class of ternary metal hydrides having a fluorite-type metal atom arrangement (for a recent list of known representatives see ref 11). It is the third known member that contains a 3d element, and it fills the gap between the two previously reported hydrides, Mg_2FeH_6[1] and Mg_2NiH_4.[9,10,12] The prominent structural feature of Mg_2CoD_5 at room temperature is the five-coordinate, square-pyramidal complex ion CoD_5^{4-}, which can be considered as a species intermediate between the six-coordinate, octahedral complex ion FeD_6^{4-} as found in Mg_2FeD_6[1] and the four-coordinate, deformed square-planar complex ion NiD_4^{4-} as found in Mg_2NiD_4.[12] Square-pyramidal complex ions based on cobalt are relatively rare, and the present compound appears to be the first example for such a complex that contains Co(I) ions. The CoD_5^{4-} unit in Mg_2CoD_5 has C_{4v} symmetry. As expected for a d^8 system of this symmetry the metal–ligand distances toward the base (d[Co–D] = 1.515 (3) Å) are significantly shorter than that toward the apex (d[Co–D] = 1.590 (17) Å), and the metal atom is displaced (by 0.20 (2) Å) from the pyramidal base toward the apex. The D–Co–D bond angle, $\theta = 165$ (1)°, between opposite basal ligands is close to the angle $\theta = 164°$ as predicted by model calculations for a d^8 system.[13] A well-known example for another square-pyramidal d^8 system having this geometry is the complex ion $Ni(CN)_5^{3-}$ (d[Ni–CN] = 1.86 Å (average basal) and 2.17 Å (apical); $\theta = 160°$[14]).

The transition-metal–deuterium distances in the CoD_5^{4-} complex (average d[Co–D] = 1.53 Å) are similar to those in the FeD_6^{4-} complex (d[Fe–D] = 1.556 Å[1]) and the NiD_4^{4-} complex (average d[Ni–D] = 1.56 Å[12]). They are consistent with the assumption of covalent interactions between the transition-metal and deuterium atoms. The shortest distances between the D atoms occur within the pyramidal base of the Co complex (d[D–D] = 2.12 Å). They are close to the limiting value of 2.10 Å as found in most other metal deuteride structures (for a recent review see ref 15). Thus repulsive interactions between the deuterium ligands are likely to contribute to the detailed geometry of the CoD_5^{4-} unit. All other D–D distances in the structure are greater than 2.34 Å (Table II). The Mg–D distances (2.17–2.40 Å) are similar to those in Mg_2FeD_6 (2.27 Å[1]) and Mg_2NiD_4 (average 2.40 Å[12]), but are significantly greater than those in binary MgD_2 (1.95 Å).

The structure of Mg_2CoD_5 at room temperature is closely related to, but not identical with, the reported low-temperature structure of Sr_2IrD_5.[2] Both compounds show the same deformation of their tetragonal metal atom sublattice, which consists of a relative expansion along c ($c/a > 2^{1/2}$). However, their lattice symmetries and in particular their D atom distributions appear to differ. In the Co compound, which has a primitive lattice, the square-pyramidal CoD_5^{4-} groups form a sequence of sheets that are perpendicular to c and point in directions opposite to each other. The Co atoms are significantly displaced from their pyramidal base. According to ref 2 the Ir compound at 4 K has a body-centered lattice with a disordered arrangement of the IrD_5^{4-} pyramids. This symmetry does not allow the Ir atoms to be displaced from their pyramidal base. In view of the relatively low resolution of the diffraction data reported by ref 2 a reinvestigation of that compound may be worthwhile. As to the high-temperature structure of Mg_2CoD_5 our neutron diffraction measurements do not allow us to draw any conclusions about the local Co atom environment.

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Mg_2CoD_5 is presumably nonmetallic, and it shows no detectable homogeneity range within experimental resolution. In view of its structural and electronic similarities to the related hydrides Mg_2NiD_4 and Mg_2FeD_6, it is reasonable to rationalize its bonding in terms of divalent magnesium cations and tetravalent hydrido–transition-metal anions that satisfy the 18-electron rule. Its relatively low magnetic susceptibility ($\chi_g = 3\ (2) \times 10^{-6}$ emu/g) favors a low-spin state for the Co(I) ions. It does not favor a high-spin state because square-pyramidal d^8 high-spin systems show relatively strong paramagnetic behavior ($\chi_g > 10 \times 10^{-6}$ emu/g as reported for compounds containing high-spin Ni^{2+}.[16] The thermal stability of Mg_2CoH_5 (86 (5) kJ/mol of H_2) is higher than that of Mg_2NiH_4 (64 kJ/mol of H_2) but lower than that of Mg_2FeH_6 (98 (3) kJ/mol of H_2). Its volume and weight efficiency for hydrogen storage (4.5 wt %, 7.5 × 10^{22} H atoms/cm^3) are intermediate between those of Mg_2NiH_4 (3.6 wt %, 5.8 × 10^{22} H atoms/cm^3) and Mg_2FeH_6 (5.4 wt %, 9.0 × 10^{22} H atoms/cm^3).

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Registry No. Mg_2CoH_5, 98586-77-7; Mg_2CoD_5, 98586-78-8; Mg, 7439-95-4; Co, 7440-48-4; H_2, 1333-74-0; D_2, 7782-39-0.

Supplementary Material Available: Tables of raw neutron diffraction data (298 K) and the results of the structure refinement including structural data for Mg_2CoD_5 and MgD_2, profile parameters, *R* factors, and background values (7 pages). Ordering information is given on any current masthead page.

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Reactions of the Dicarbonyl Complex $Re_2Cl_4(dppm)_2(CO)_2$ with Nitriles and Isocyanides. Synthesis of $[Re_2Cl_3(dppm)_2(CO)_2L]^{n+}$ (n = 0, 1; L = RCN, RNC) and the Structural Characterization of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$

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The dicarbonyl complex $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)$ (dppm = bis(diphenylphosphino)methane) reacts with nitriles (RCN) and isocyanides (RNC) in the presence of $TlPF_6$ to generate cations of stoichiometry $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = CH_3CN, C_2H_5CN, C_6H_5CN, Me_2CHNC, Me_3CNC). These complexes exhibit a well-defined electrochemistry including a chemically accessible reduction ($E_{1/2} \simeq -0.1$ V vs. Ag/AgCl). The reactions of cobaltocene with these salts produce the paramagnetic neutral complexes $Re_2Cl_3(dppm)_2(CO)_2L$, the first examples of multiply bonded dirhenium complexes that possess the Re_2^{3+} core. The nitrile compound $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6 \cdot CH_2Cl_2 \cdot {}^1/_2(C_2H_5)_2O$ has been characterized by X-ray crystallography. It forms crystals in space group $P\bar{1}$ with Z = 2 and the following unit cell dimensions: a = 16.574 (5) Å, b = 17.617 (6) Å, c = 12.238 (3) Å, α = 101.94 (2)°, β = 107.64 (2)°, γ = 65.54 (2)°, V = 3086 (2) Å^3. The cation is an edge-sharing bioctahedron with one bridging CO and one bridging Cl. The central plane containing the shared edge has the EtCN, μ-CO, and CO ligands along one side and three Cl atoms along the other. The bridging bidentate dppm ligands occupy the positions above and below this plane. The Re–Re distance is 2.586 (1) Å, the average Re–P distance is 2.472 [5] Å, the Re–CO(terminal) distance is 1.92 (2) Å, and the two Re–CO(bridge) distances are 2.00 (2) and 2.13 (2) Å. The Re–Cl(bridge) distances, 2.473 (5) and 2.448 (4) Å, are longer than the Re–Cl(terminal) distances, 2.407 (5) and 2.419 (5) Å, as expected. This structure provides further insight into the structure of the $Re_2Cl_4(dppm)_2(CO)_2$ molecule, which forms systematically disordered crystals.

Introduction

Studies involving the reactions of the electron-rich triply bonded complex $Cl_2Re(\mu\text{-}dppm)_2ReCl_2$ (dppm = bis(diphenylphosphino)methane) are presently being conducted in our laboratory. This compound displays a surprising reactivity toward nitriles and pyridine,[2] as well as toward isocyanide ligands[3] and carbon monoxide.[4] The carbonylation reactions of $Re_2Cl_4(dppm)_2$ led to the discovery of the fluxional molecules $Re_2Cl_4(dppm)_2(CO)_n$ (n = 1, 2), the first examples of dinuclear carbonyl derivatives of this type in which a M–M bond is retained.[4] The green dicarbonyl species was shown by X-ray crystallography to possess the edge-shared bioctahedral structure $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)$. However, due to a disorder problem it was not possible to distinguish between a cis and trans disposition of the bridging and terminal carbonyl groups.[4]

As part of our efforts to develop the chemistry of this unusual dicarbonyl complex, we investigated its reactivity with the intent of preparing derivatives that could be readily characterized and that would in turn allow us to ascertain the stereochemistry of the carbonyl ligands. Although this molecule is relatively unreactive under ordinary conditions, it can be induced to undergo substitution reactions with a variety of ligands in the presence of $TlPF_6$. In the present report we describe the synthesis and characterization of the diamagnetic salts $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = RCN, RNC) together with some details of the analogous paramagnetic neutral complexes, which are prepared by the cobaltocene reductions of the monocations. The latter species constitute the first examples of dirhenium complexes that possess the Re_2^{3+} core. The results of a single-crystal X-ray diffraction study of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ are also described.

Experimental Section

Starting Materials. The complex $Re_2Cl_4(dppm)_2(CO)_2$ was prepared as previously described from the reaction of $Re_2Cl_4(dppm)_2$ with carbon monoxide in dichloromethane.[4] Nitriles and other common solvents were obtained from commercial sources and were stored over molecular sieves. The *tert*-butyl and isopropyl isocyanide ligands were prepared according to a standard literature procedure.[5] Bis(diphenylphosphino)methane

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