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Communication

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Counterion Influence on the Vibrational Wavenumbers in Ternary and Quaternary Metal Hydride Salts, A_2MH_6 (A = Alkali Metal, Alkaline Earth, and Lanthanides; M = Ir, Fe, Ru, Os, Pt, Mn)

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S *Supporting Information*

ABSTRACT: The wavenumbers of the ν_3 metal–hydrogen stretching mode (T_{1u}) in the IR spectra of both ternary and quaternary hexahydrido salts of transition metals from groups 7 to 10 ($[Mn^{I}H_6]^{5-}$, $[Fe^{II}H_6]^{4-}$, $[Ru^{II}H_6]^{4-}$, $[Os^{II}H_6]^{4-}$, $[Ir^{III}H_6]^{3-}$, and $[Pt^{IV}H_6]^{2-}$) depend linearly upon the ionization energies of the counterions (alkali metal, alkaline earth, and lanthanide) with a separate line for each metal. This relationship provides quantitative support for the charge-transfer mechanism for explaining the stabilities of these compounds.

The search for compounds with potential use as hydrogen-storage materials has included transition-metal hydride salts such as Mg_2FeH_6, which has a high volume density but the disadvantage of high stability.[1,2] The structure and spectroscopic properties of this compound have been reported[3,4] as have the preparation, structures, and properties of other group 8 transition-metal hydride salts with alkaline earths and lanthanides (A_2MH_6, where M = Ru, Os and A = Mg, Ca, Sr, Ba. Eu, Yb).[5−9] The vibrational spectroscopic properties of a wide range of metal hydrides have been reviewed by Parker.[10] Useful information can be obtained from studies of trends in vibrational spectra, and Kritikos and Noréus[6] showed that the wavenumbers of the intense IR absorption band (ν_3, T_{1u}) in these ternary metal hydride complexes correlated with the unit cell dimensions, with a different line for each central metal atom. Recently, this dependence on unit cell dimensions has been extended in a study of quaternary metal hydrides (QMHs) of iridium, $AAeIrH_6$ (A = Na, K and Ae = Ca, Ba, Eu) with octahedral coordination[11] and cubic K_2PtCl_6-type crystal structures. Normally, the hydrido compounds of group 9 transition metals, $A_2[Ir(I)H_5]$ and $A_2[Rh(I)H_5]$, are pentacoordinated square-pyramidal structures,[5,12−15] and these new hexacoordinated iridium(III) compounds allow a comparison with the spectroscopic properties of the salts of the group 8 transition metals. The correlation with the IR wavenumbers is now with the inverse of the unit cell parameter, but for the osmium and ruthenium salts, the values of the wavenumbers for compounds with magnesium do not follow the trends shown by other alkaline-earth or lanthanide salts.

A transfer of charge from the hydrido anion to the counterion has been suggested as a mechanism of stabilizing the ternary metal hydride salts.[6,11,16,17] In the case of Mg_3RuH_3, theoretical calculations demonstrate the particular role of magnesium in stabilizing that structure.[17] Because the reduced masses are close to unity (due to the heavy-atom mass), the trends in the frequencies of vibration depend essentially upon the differences in the force constants of the metal hydrogen bond, i.e., a localized bond effect, and a more appropriate explanation of the trends in the series of transition-metal hydride salts is necessary. The extent of charge transfer, being dependent on the ability of the cations to accept charge, should depend upon the ionization energy of the cation. Full assignments of the Raman, IR, and inelastic neutron scattering spectra of the hexahydridoruthenium salts have been reported, including a resolution of the complex region around the ν_3 IR band,[8,9] and it was shown that a linear dependence occurs for plots of the ν_3 wavenumbers versus the second ionization energies of the counterion,[7] with separate parallel lines for the ruthenium and osmium compounds. Moreover, a single line was obtained when the wavenumbers were plotted versus the sum of the second ionization of the cation and the ionization energy of the central metal atom. Figure 1 shows plots for the series of TMH salts also including the magnesium and calcium salts[4,18] of $[FeH_6]^{4-}$ and the alkali-metal salts[16,19,20] of $[PtH_6]^{2-}$. Separate straight lines result for each transition

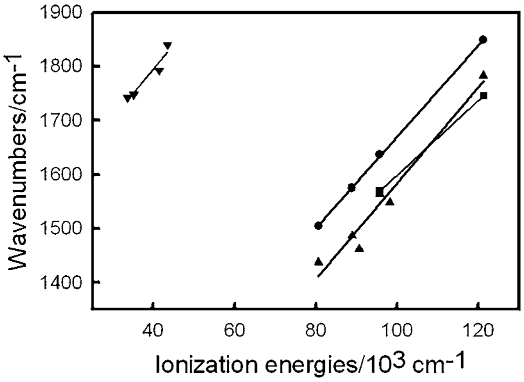

Figure 1. Ternary metal hydrides. Wavenumber dependence on the ionization energy (cm^{-1}) of the counterion. Platinum: inverted triangles. Ruthenium: triangles. Osmium: circles. Iron: squares.

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metal, and the values for Mg_2RuH_6 and Mg_2OsH_6 now lie on the lines and no longer appear to be anomalous, as they were for plots of wavenumbers versus unit cell dimensions[6] or the reciprocal of the unit cell parameter.[11] Least-squares fits to the data gave the intercepts and slopes listed in Table 1, together with the R^2 factors. For the group 8 metals, a common line is again found when the ionization energies of the central metal atom are included, and the value reported[17] for the calcium salt of $[FeH_6]^{4-}$ is on the line, but the value for Mg_2FeH_6 is low. Curiously, a calculated value[21] of ν_3 (1794 cm^{-1}) places this point on the line.

Table 1. Intercepts (cm^{-1}) and Slopes ($\times 10^3$) of the Wavenumber Dependence on Ionization Energies (Note: Only Two Points Were Available for $[FeH_6]^{4-}$ and $[MnH_6]^{5-}$)

	intercept	slope	R^2
A_2FeH_6	910	6.57	
A_2RuH_6	693	8.90	0.961
A_2OsH_6	822	8.47	0.999
A_2PtH_6	1428	9.18	0.928
$RMnMnH_6$	717	5.57	
$AAeIrH_6$	117	11.2	0.961
$CaEuRuH_6$	−336	19.9	0.992
$SrEuRuH_6$	671	9.16	0.926

With the newly reported data for the $[IrH_6]^{3-}$ salts, this approach can be extended to QMHs. In the case of the QMHs of iridium, the average of the first ionization energy of the alkali metal (Na or K) and the second ionization energy of the alkaline earth or lanthanide (Ca, Sr, Ba, or Eu) was used, and for a series of mixed salts of ruthenium with varying relative proportions of calcium and europium and strontium and europium[22] (see the Supporting Information), the second ionization energies of calcium, strontium, and europium were weighted according to their mole fractions. Hydrides of the type RMn_2H_6, which also have the K_2PtCl_6 structure and are formulated as $RMn[MnH_6]$, where R is Y or Er, have been reported[23] but with limited IR spectroscopic data. The ionization energy used for these compounds was the average of the third ionization energy of yttrium or erbium and the second ionization energy of manganese. Figure 2 shows the dependence of the wavenumbers on the ionization energy for each of these series, and straight-line dependences were again observed.

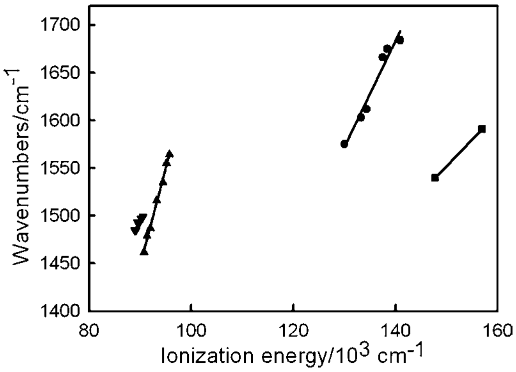

Figure 2. QMHs. Wavenumber dependence on the ionization energies (cm^{-1}). CaEu/Ru: triangles. SrEu/Ru: inverted triangles. Iridium: circles. Manganese: squares.

The values of the intercepts, slopes. and R^2 factors are included in Table 1.

The fact that a wide variety of QMH salts also show a dependence of wavenumbers on ionization energies is additional support for the charge-transfer mechanism and suggests the possibility of "tuning" the stability of metal hydride salts by an appropriate choice of the counterions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of wavenumbers used in Figures 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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