Registry No. Cu(diEten)$_2$$^{2+}$, 52918-69-1; Cu(adiEten)$_2$$^{2+}$, 46754-10-3; Cu(Meen)$_2$$^{2+}$, 36421-64-4; Cu(C-Meen)$_2$$^{2+}$, 17992-12-0; Cu(C,C-diMeen)$_2$$^{2+}$, 52918-70-4.

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A Case for Covalent Bonding in Lanthanide Trihalides

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Many of the properties of lanthanide compounds, particularly complexes, have been interpreted as supporting the argument that bonding to the lanthanide atom is substantially electrostatic.[1] However, there have been suggestions that covalent bonding may be important in chelates,[2] and a pyramidal structure has been suggested for PrF_3,[3] which would not be expected if bonding were purely ionic. In addition, it has been shown that covalent bonding must be invoked to account for the observed dissociation energies of LnX (X = O, S, Se, Te) molecules,[4] and a σ-bonded lutetium alkyl has recently been prepared and its structure established by X-ray diffraction.[5]

An appropriate model for bonding in the lanthanide trihalide molecules should account for the bond strength of these molecules. Thermodynamic and spectral data in the literature provide a basis for calculations testing the ionic model and assessing whether a covalent model may be appropriate. The approach used here is to calculate atomization energies of the molecules and to apply first an ionic model and then a covalent model in an attempt to account for observed trends, these models being considered the only reasonable ones for these molecules.

Atomization energies of LnX_3 molecules may be calculated from the thermochemical cycle

$$\begin{array}{ll}
LnX_3(s) = Ln(s) + {}^3/_2X_2(\text{std state}) & -\Delta H_f(LnX_3) \\
LnX_3(g) = LnX_3(s) & -\Delta H_s(LnX_3) \\
Ln(s) = Ln(g) & \Delta H_s(Ln) \\
{}^3/_2X_2(\text{std state}) = 3X(g) & \Delta H_f(X) \\
\hline
LnX_3(g) = Ln(g) + 3X(g) & \Delta H_{at}
\end{array}$$

The data and results of such calculations are given in Table I,[6–19] the values for all entries being at 298.15°K. All entries are rounded to the nearest kilocalorie, and estimated quantities are in parentheses. The assumed uncertainty is ±5 kcal if all quantities are measured and ±10 kcal if one or more estimated values are used. The double periodicity in atomization energy as a function of atomic number has also been noted for the enthalpies of sublimation of the metals[7] (see Table I) and for the dissociation energies of monochalconide molecules.[4,20,21]

The ionic model was assessed in terms of the processes

$$\begin{array}{ll}
Ln^{3+}(X^-)_3(g) = Ln^{3+}(g) + 3X^-(g) & -\Delta H_{ia} \\
Ln^{3+}(g) + 3e^- = Ln(g) & -\Sigma IP \\
3X^-(g) = 3X(g) + 3e^- & 3EA \\
\hline
Ln^{3+}(X^-)_3(g) = Ln(g) + 3X(g) & \Delta H_{at}'
\end{array}$$

The ion association energies were calculated assuming trigonal-planar geometry (even though PrF_3 is probably not planar). Interionic distances were estimated using the measured value[22] for LaF_3 and Pauling's crystal radii,[23] assuming a constant ratio between the sum of the crystal ionic radii and the interionic distance in the gaseous molecule.[14] The relationship used for the calculation was

$$\Delta H_{ia} = \left\{\left[-3\left(\frac{3e^2}{r}\right) + \frac{3e^2}{r\sqrt{3}}\right]\left(1 - \frac{1}{n}\right)\right\}N_0$$
$$= \frac{1}{r\,(\text{Å})}\left(1 - \frac{1}{n}\right)(2.413 \times 10^3 \text{ kcal Å/mol})$$

where r is the interionic distance, e is the electronic charge, n is the Born exponent (9.5 for LnF_3, 10.5 for $LnCl_3$, 11.0 for $LnBr_3$, and 12.0 for LnI_3), and N_0 is the Avogadro number. Ionization potentials are from the compilation of Martin and coworkers,[24] and electron affinities are values cited by Huheey.[25]

The results of the calculations using the ionic model are given in Table II. Differences between ΔH_{298} (thermochemical values) and ΔH_0 (ionic model) have been neglected. Comparison of values of $\Delta H_{at}'$, calculated from the ionic model, with values of ΔH_{at} based on thermochemical data shows that the ionic model does not account for the observed atomization energies. Furthermore, the discrepancies increase from LnF_3 to LnI_3. This is most clearly seen in the ratio $\Delta H_{at}'/\Delta H_{at}$. For the LnF_3 molecules the ionic model accounts for 80–90% of the observed atomization energy, but for the LnI_3 molecules this drops to as low as 27%. Not surprisingly, the ionic model works best for LnF_3 molecules, but in addition to increasing departure from ionic behavior with $LnCl_3$, $LnBr_3$, and LnI_3 molecules, the extent to which the ionic model accounts for the observed atomization energies itself shows a double periodicity with minima at EuX_3 and YbX_3. While choosing shorter interionic distances could increase the magnitude of ΔH_{ia} and hence increase $\Delta H_{at}'$, the trend of increasing departure from the ionic model and the double periodicity would remain.

Since the ionic model is seen to have serious deficiencies, the question arises as to whether a covalent model would be any better. This question cannot be answered in full at present because of the complexities of theoretical calculations. However, an assessment can be made as to whether a covalent perspective will account for the observed trends in atomization energies, in particular the double periodicity noted above. The approach used is to calculate atomization energies, not to the

Table I. Atomization Energies (kcal)

		LnF$_3$: ΔH_f(F) = 18.86[a]			LnCl$_3$: ΔH_f(Cl) = 28.992[a]			LnBr$_3$: ΔH_f(Br) = 26.740[a]			LnI$_3$: ΔH_f(I) = 25.537[a]		
Ln	ΔH_s-(Ln)[b]	$-\Delta H_f$-(LnF$_3$)[d]	ΔH_s-(LnF$_3$)[e]	ΔH_{at}-(LnF$_3$)	$-\Delta H_f$-(LnCl$_3$)[i]	ΔH_s-(LnCl$_3$)[k]	ΔH_{at}-(LnCl$_3$)	$-\Delta H_f$-(LnBr$_3$)[l]	ΔH_s(LnBr$_3$)[l]	ΔH_{at}-(LnBr$_3$)	$-\Delta H_f$-(LnI$_3$)	ΔH_s(LnI$_3$)[n]	ΔH_{at}-(LnI$_3$)
La	103	405	107[f]	458	256	80	366	(213)	82[m]	316	167[l]	80[m]	260
Ce	100[c]	(413)	106[g]	463	252	79	359	(209)	78[m]	313	164[l]	79	258
Pr	89	401	107[h]	440	253	78	351	(208)	77[m]	304	162[l]	79	244
Nd	78	395	95	439	246	77	334	(203)	77[m]	291	159[l]	78	229
Pm													
Sm	49	(401)	107	399	245	75	305	(200)	(73)	256	153[i]	(70)[l]	209
Eu	42	(398)	100	397	247	75	301	(199)	(72)	249	(147)[l]	(70)[l]	195
Gd	96	389	98	443	240	74	349	(197)	(72)	301	148[i]	70	249
Tb	94	(392)	111	438	238[j]	70	349	(194)	(71)	297	(143)[l]	68	246
Dy	71	(388)	115	400	238	69	327	(192)	(70)	273	144[i]	69	223
Ho	71	(384)	116	397	240[j]	68	330	(190)	(70)	271	142[i]	72	216
Er	82	378	120	396	229	68	330	(187)	(69)	280	140[i]	69	229
Tm	59	(376)	99	393	236	67	315	(185)	(68)	256	139[i]	(66)[l]	207
Yb	36	(372)	95	370	229	67	286	(183)	(68)	232	(134)[l]	(66)[l]	181
Lu	102	(369)	103	425	228	67	350	(180)	(68)	295	133[i]	(66)[l]	246

[a] Reference 6. [b] Reference 7, unless otherwise noted. [c] Reference 8. [d] Measured values from ref 9; estimated values from ref 10. [e] Reference 11, unless otherwise noted. [f] Reference 12. [g] Reference 13. [h] Reference 14. [i] Reference 15, unless otherwise noted. [j] Reference 16. [k] Reference 17. [l] Reference 10, unless otherwise noted. [m] Reference 18. [n] Reference 19, unless otherwise noted.

Table II. Ionic Model[a]

		LnF$_3$: 3EA = 239 kcal			LnCl$_3$: 3EA = 250 kcal			LnBr$_3$: 3EA = 233 kcal			LnI$_3$: 3EA = 212 kcal		
Ln	ΣIP	$-\Delta H_{ia}$	$\Delta H_{at}'$	$\Delta H_{at}'/\Delta H_{at}$	$-\Delta H_{ia}$	$\Delta H_{at}'$	$\Delta H_{at}'/\Delta H_{at}$	$-\Delta H_{ia}$	$\Delta H_{at}'$	$\Delta H_{at}'/\Delta H_{at}$	$-\Delta H_{ia}$	$\Delta H_{at}'$	$\Delta H_{at}'/\Delta H_{at}$
La	826	978	391	0.85	840	264	0.72	804	211	0.67	784	170	0.65
Ce	842	996	393	0.85	850	258	0.72	816	207	0.66	793	163	0.63
Pr	867	1000	372	0.85	856	239	0.68	826	192	0.63	799	144	0.59
Nd	884	1005	360	0.82	860	226	0.68	829	178	0.61	802	130	0.57
Pm													
Sm	925	1024	338	0.85	870	195	0.64	841	149	0.58	811	98	0.47
Eu	965	1028	302	0.76	874	159	0.53	845	113	0.45	814	61	0.31
Gd	896	1034	377	0.85	877	231	0.66	848	185	0.61	817	133	0.53
Tb	906	1039	372	0.85	885	229	0.66	851	178	0.60	822	128	0.52
Dy	932	1043	350	0.88	888	206	0.63	854	155	0.57	826	106	0.48
Ho	938	1054	355	0.89	891	203	0.62	857	152	0.56	829	103	0.48
Er	940	1058	357	0.90	895	205	0.62	860	153	0.55	832	104	0.45
Tm	967	1064	336	0.85	898	181	0.57	864	130	0.51	835	80	0.39
Yb	1002	1070	307	0.83	903	151	0.53	867	98	0.42	838	48	0.27
Lu	929	1072	382	0.90	906	227	0.65	870	174	0.59	841	124	0.50

[a] IP and ΔH values in kilocalories.

ground state of the lanthanide atom, but to the excited state having the same electronic configuration as proposed for the covalently bonded lanthanide. In order to form three covalent bonds there must be three unpaired electrons in appropriate orbitals. Assuming the f orbitals not to be involved in bonding, atomization energies were calculated for LnX$_3$ molecules to give the lanthanide atom in the d^{2}s state since this state, except for Lu, is the state of lowest energy having three non-f unpaired electrons. This atomization energy to Ln(d^{2}s) was calculated by adding the promotion energy (d^{2}s ← ground state) for each lanthanide[26] to the thermochemical atomization energy. The results are summarized in Table III.

Except for the discontinuity at EuX$_3$ in every case, the atomization energies to Ln(d^{2}s) are a rather smooth function of atomic number within assumed uncertainty limits of ±5 kcal if all thermochemical quantities are measured and ±10 kcal if one or more thermochemical quantities is estimated. That is, the double periodicity has been removed by taking the promotion energy into account. The curve is smoothest for the chlorides for which measured data are most complete, and apparent discontinuities in other curves are well within assumed uncertainty limits. There are two possible sources of the discontinuity at EuX$_3$. The difficulty is most likely in the properties of Eu, since the discontinuity is present in every trihalide series. The promotion energy for Eu given by Brewer[26] is an estimate and is thus a possible source of the discontinuity. Another possible source of error is that the enthalpy of sublimation of europium[7] may be too high due perhaps to the effects of dissolved oxygen.

Table III. Covalent Model[a]

Ln	P(f^{n-3}-d^{2}s)[b]	ΔH^*-(LnF$_3$)[c]	ΔH^*-(LnCl$_3$)[c]	ΔH^*-(LnBr$_3$)[c]	ΔH^*-(LnI$_3$)[c]
La	8	466	374	324	268
Ce	7	470	366	320	265
Pr	20	460	371	324	264
Nd	25	464	359	316	254
Pm					
Sm	55	454	360	311	264
Eu	86	483	387	335	281
Gd	18	461	367	319	267
Tb	23	461	372	320	269
Dy	49	449	376	322	272
Ho	54	451	384	325	270
Er	57	453	387	337	286
Tm	79	472	394	335	286
Yb	114	484	400	346	295
Lu	54	479	404	349	300

[a] All values in kilocalories. [b] Reference 26. [c] Atomization energy to Ln(d^{2}s).

Additional support for a covalent model comes from a comparison of differences in bond energies: $[\bar{D}(\mathrm{LnF_3}) - \bar{D}(\mathrm{LnCl_3})] = 30 \pm 5$ kcal, $[\bar{D}(\mathrm{LnCl_3}) - \bar{D}(\mathrm{LnBr_3})] = 17 \pm 3$, and $[\bar{D}(\mathrm{LnBr_3}) - \bar{D}(\mathrm{LnI_3})] = 18 \pm 3$ kcal. These compare favorably with corresponding differences in covalently bonded metal and nonmetal halides:[27] $[\bar{D}(\mathrm{AF}_n) - \bar{D}(\mathrm{ACl}_n)] = 20$–$50$ kcal, $[\bar{D}(\mathrm{ACl}_n) - \bar{D}(\mathrm{ABr}_n)] = 15 \pm 5$ kcal, and $[\bar{D}(\mathrm{ABr}_n) -$

$\bar{D}(\mathrm{AI}_n)$] = 16 ± 3 kcal, where A = Al, Si, Ge, Sn, Pb, As.[28,29]

It is concluded that a covalent model involving d^2s hybrid orbitals on the lanthanide provides a better basis for understanding the thermochemical atomization energies of the lanthanide trihalides than does the ionic model. However, more work, both theoretical and experimental, is obviously needed. With respect to the latter, a redetermination of the enthalpy of sublimation of europium would seem to have high priority, followed closely by enthalpies of formation and sublimation of the bromides as well as determination of missing values for the other halides. Hopefully, atomic and molecular spectroscopic studies will provide additional clarification.

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Tungsten Carbonyl Complexes as Ligands

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Phosphorus–phosphorus coupling through a metal atom in complexes containing two chemically nonequivalent phosphorus atoms may be measured directly from the ^{31}P spectrum of the complex.[3,4] If the phosphorus atoms are chemically equivalent, however, this direct approach is not possible although the value of the coupling constant can often be obtained from the ^{1}H spectrum of the complex by band shape analysis, by use of double resonance techniques, and in some instances by observation of weak-intensity ($\chi = 1$) wing peaks.[5-9] Values of $^2J_{PP}$ reported for cis square planar complexes of platinum(II), $(R_3P)_2PtCl_2$, have all been obtained by computer simulation techniques and this method has been shown to be somewhat unreliable.[5] In this study we have utilized the unique ligand, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, to obtain $^2J_{PP}$ for the chemically equivalent phosphorus nuclei in the complex *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$.

In addition, the ligating properties of $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ have been further examined by isolating and characterizing the complexes $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$ and $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$.

Experimental Section

Phosphorus-31 nmr spectra were recorded with a Varian XL-100 spectrometer equipped with Fourier transform and a pulsed deuterium lock. The samples were examined in 12-mm tubes and 2.5 ml of $CDCl_3$ was used for solvent and lock. Phosphoric acid (85%) in a 1.0-mm capillary was suspended in the sample as an external reference. Coupling constants are accurate to ±0.1 Hz. Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 infrared spectrometer. These spectra were expanded with an E. H. Sargent recorder and are considered accurate to $\pm 2\ \mathrm{cm}^{-1}$. Polystyrene was used as a frequency standard and chloroform was used as a solvent for each measurement. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparations. The ligand, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, was prepared as previously described.[10]

***cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$ and $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$.** To 50 ml of ethanol were added $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (1.03 g, 0.00143 mol) and K_2PtCl_4 (0.3 g, 0.0007 mol). The reaction mixture was stirred for 2 days at 35° after which time all traces of the red K_2PtCl_4 had disappeared. The fine white precipitate which resulted was washed with water and recrystallized from a 50% methanol–dichloromethane solution to give 0.3 g of white crystals which were found to decompose at 191–194°. *Anal.* Calcd for $C_{62}H_{48}O_{10}P_4W_2PtCl_2$: C, 43.53; H, 2.83; P, 7.24; Cl, 4.15. Found: C, 43.18; H, 2.70; P, 7.14; Cl, 4.30. The filtrate was taken to dryness and to the residue was added 20 ml of water. The water mixture was extracted with 10 ml of dichloromethane. To the dichloromethane was added an equal volume of methanol. The solution was heated on a steam bath until the volume was halved. Upon sitting for 12 hr, 0.2 g of the oxide complex, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, precipitated. The compound was found to decompose at 170–175°. *Anal.* Calcd for $C_{31}H_{24}P_2O_6W$: C, 50.43; H, 3.28; P, 8.39. Found: C, 50.15; H, 3.26; P, 8.22.

$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$. To 50 ml of absolute ethanol were added $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (0.50 g, 0.0069 mol) and $HgCl_2$ (0.19 g, 0.00070 mol). The solution became cloudy immediately. The mixture was stirred for 18 hr. Upon filtering the mixture 0.52 g of white crystals were collected. These were recrystallized with a 50% methanol–dichloromethane solution to give 0.41 g of the mercury–tungsten complex. The complex was found to decompose at 183–185°. *Anal.* Calcd for $C_{62}H_{48}P_4Hg_2W_2Cl_4O_{10}$: C, 37.46; H, 2.43; P, 6.23; Cl, 7.13. Found: C, 37.08; H, 2.50; P, 6.15; Cl, 6.97.

Results and Discussion

The structure of $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ has been previously established with ^{31}P nmr and its ligating tendencies have been demonstrated with the preparation of the quaternized product $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6^-]$ and the bimetallic product $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2W(CO)_5$.[10,11] In various organic