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Correction to "Quantifying the σ and π Interactions between U(V) f Orbitals and Halide, Alkyl, Alkoxide, Amide and Ketimide Ligands"

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While preparing a follow-up manuscript, we found an error in one of the orbital reduction factors used in our crystal field models, given in Scheme 2. The third equation in that scheme was published as $k_{a_2t_2} = 1 - \frac{1}{2}N'^2\alpha_\pi'^2$; however, the correct formula is $k_{a_2t_2} = 1 - \frac{1}{2}N'\alpha_\pi'^2$.

All analyses have been redone using the correct orbital reduction factors. The main impact is that the correction factor for the f-orbital screening by covalent bonding to the ligands is reduced from 0.96 to 0.94. In addition, the fits using the MO-RSO model are slightly poorer than when using the incorrect version of the orbital reduction factor, which are reflected in slightly higher uncertainties for the values used in the model. Fits using the MO-T model are only slightly affected by the change in the orbital reduction factor. The values of parameters in either model (θ, Δ, α_σ^2, and $\alpha_\pi'^2$) change very little for any of the complexes. In almost all cases, the new values are equal to the old values within error. As a result, the covalency and strengths of the σ and π bonds between the ligands and f-orbitals, which are the main focus of this publication, are almost unchanged when using the correct orbital reduction factor. The conclusions reached in the paper are unaffected by the use of the incorrect version of the orbital reduction factor.

The corrected portions of the Article, including text, Scheme 2, and Tables 2−5, are given below with the corrections underlined. (See the original Article for cited references and SI.)

Page 10745, the full paragraph of text below the schemes should read as follows:

The relationship between ζ_f and the free ion value, $\zeta_{\text{free-ion}}$, must be determined before the MO-RSO model can be applied. As noted above, ζ_f should be slightly smaller than $\zeta_{\text{free-ion}}$ due to screening of the f orbitals caused by covalent bonding between the ligands and the s, p, and d orbitals of the metal center. The value of $\alpha_\pi'^2$ is particularly sensitive to ζ_f; therefore, one would like to use the spectroscopically determined value of $\alpha_\pi'^2$ to calibrate ζ_f. The only f^1 complex for which this parameter has been evaluated is NpF_6 where $\alpha_\pi'^2$ has been determined to be 0.044(3) from the degree of ^{19}F hyperfine coupling observed by EPR.[28] When the MO-RSO model is applied to NpF_6 with $\alpha_\pi'^2$ fixed at 0.044, the best fit is obtained with ζ_f = <u>2518</u> cm^{-1}. Since the calculated spin−orbit coupling constant of Np(VI) is 2666 cm^{-1},[44] ζ_f = <u>0.94</u> $\zeta_{\text{free-ion}}$. This relationship will be used to determine ζ_f using the calculated values of $\zeta_{\text{free-ion}}$.[44] The effect of using ζ_f = <u>0.94</u> $\zeta_{\text{free-ion}}$ rather than ζ_f = $\zeta_{\text{free-ion}}$ is relatively small: the value of $\alpha_\pi'^2$ is decreased by ∼0.025 and the value of Δ is decreased by ∼100 cm^{-1} (Table S1). The 4% decrease in the value of ζ_f due to covalent bonding between the ligands and the s, p, and d orbitals is slightly larger than the 1.7% decrease estimated for the reduction in the 3d SO coupling in $KNiF_6$ due to covalent bonding between the ligands and the nickel s and p orbitals.[41]

Scheme 2. Orbital Reduction Factors for an Octahedral f^1 Complex

$$k_{t_1t_1} = 1 - N^2\left[\frac{4}{3}\alpha_\pi^2 + \alpha_\sigma^2 + \frac{2\sqrt{2}}{3}\alpha_\pi\alpha_\sigma\right]$$

$$k_{t_2t_2} = 1 - 2N'^2\alpha_\pi'^2$$

$$\underline{k_{a_2t_2} = 1 - \frac{1}{2}N'\alpha_\pi'^2}$$

$$k_{t_1t_2} = 1 - NN'\left[\frac{1}{2}\left(\alpha_\pi^2 + \alpha_\pi'^2 + \alpha_\sigma^2\right) + \sqrt{\frac{2}{15}}\alpha_\pi'\left(\alpha_\sigma - \frac{\alpha_\pi}{\sqrt{2}}\right)\right]$$

Table 2. Experimental NIR Data and Modeled Results for Octahedral f[1] Complexes[a]

	model	Γ_8 (cm^{-1})	$\Gamma_{7'}$ (cm^{-1})	$\Gamma_{8'}$ (cm^{-1})	Γ_6 (cm^{-1})	g
CeCl$_6$$^{3-}$	expt[53]	571	2161	2663	3050	−1.266
	MO-RSO	575	2161	2663	3049	−1.266
	MO-T	571	2161	2663	3050	−1.266
	CF	573	2161	2665	3048	−1.266
PaCl$_6$$^{2-}$	expt[45,49]	2108	5250	7272	8173	−1.142
	MO-RSO	2120	5551	7212	8202	−1.143
	MO-T	2149	5252	7215	8211	−1.141
	CF	1984	5287	7105	8322	−1.138
UF$_6$$^-$	expt[36,50,27]	5363	7400	13800	15900	−0.708
	MO-RSO	5401	7367	13772	15920	−0.708
	MO-T	5363	7400	13800	15900	−0.708
	CF	5111	7483	13438	16241	−0.701
UCl$_6$$^-$	expt[36,48]	3800	6794	10137	11520	−1.12
	MO-RSO	3821	6787	10106	11540	−1.12
	MO-T	3800	6794	10137	11520	−1.12
	CF	3090	6764	9902	11916	−1.10
UBr$_6$$^-$	expt[36,48]	3700	6830	9761	10706	−1.21
	MO-RSO	3710	6811	9748	10715	−1.21
	MO-T	3700	6830	9761	10706	−1.21
	CF	2705	6731	9419	11289	−1.19
U(OR)$_6$$^-$	expt[32]	4873	7094	11221	13261	−0.73
	MO-RSO	4740	7135	11396	13261	−0.73
	MO-T	4790	7087	11363	13173	−0.73
	CF	4329	7116	11235	13414	−0.72
U(NR$_2$)$_6$$^-$	expt[34]	–	6836	11181	13106	−1.15
	MO-RSO	3894	6836	11181	1306	−1.15
	MO-T[b]	–	–	–	–	–
	CF	3411	6884	10883	13325	−1.15
U(NCR$_2$)$_6$$^-$	expt[35]	3240	6112	10234	12116	−1.22
	MO-RSO	3176	6157	10283	12082	−1.22
	MO-T	3240	6112	10234	12116	−1.22
	CF	3026	6137	10008	12339	−1.21
UR$_6$$^-$	expt[31]	–	6832	10920	13436[c]	−1.43
	MO-RSO	2887	6964	10919	13436	−1.41
	MO-T[b]	–	–	–	–	–
	CF	2750	6832	10917	13666	−1.43
NpF$_6$	expt[28,38,54]	7610	9355	24000	27000	−0.605
	MO-RSO	7653	9322	23987	27011	−0.606
	MO-T	7610	9355	24000	27000	−0.605
	CF	7466	9272	23343	27622	−0.596

[a]Energies of the transitions for the halide complexes are taken from ref 19, except for those of Cs$_2$NaCeCl$_6$, which were taken from ref 53. [b]Too few data available to apply the MO-T model. [c]Error is estimated to be 1000 cm^{-1} rather than 100 cm^{-1}.

Table 3. Parameters Obtained by Fitting the NIR Spectra of Octahedral f^1 Complexes[a]

	model	θ (10^3 cm^{-1})	Δ (10^3 cm^{-1})	α_σ^2	$\alpha_\pi'^2$	ζ_f (10^3 cm^{-1})[b]
CeCl$_6$$^{3-}$	MO-RSO	0.7(2)	0.39(6)	0.00(3)	0.01(4)	0.627
	MO-T	0.7(3)	0.4(2)	0.0(1)	0.0(2)	0.63(8)
	CF	0.7(1)	0.40(3)	–	–	0.63(3)
PaCl$_6$$^{2-}$	MO-RSO	2.1(5)	1.6(2)	0.04(4)	0.04(4)	1.588
	MO-T	4.0(2)	0.0(2)	0.30(8)	0.25(3)	1.70(4)
	CF	2.3(3)	1.53(9)	–	–	1.51(5)
UF$_6$$^-$	MO-RSO	7.8(2)	3.8(1)	0.13(3)	0.04(1)	2.042
	MO-T	7.8(2)	3.7(2)	0.26(7)	0.06(4)	2.04(8)
	CF	7.0(6)	4.0(3)	–	–	2.0(1)
UCl$_6$$^-$	MO-RSO	5.0(3)	1.8(1)	0.19(3)	0.06(2)	2.042
	MO-T	5.1(5)	1.6(4)	0.4(1)	0.07(6)	2.02(4)
	CF	4.1(8)	2.1(3)	–	–	1.9(2)
UBr$_6$$^-$	MO-RSO	5.3(3)	1.0(2)	0.28(6)	0.10(3)	2.042
	MO-T	5.5(4)	0.5(4)	0.9(2)	0.13(4)	2.1(1)
	CF	4(1)	1.7(5)	–	–	1.9(2)
U(OR)$_6$$^-$	MO-RSO	5.3(5)	3.5(2)	0.13(7)	0.06(3)	2.042
	MO-T	5.0(5)	3.7(3)	0.3(2)	0.00(8)	1.9(1)
	CF	4.7(6)	3.8(2)	–	–	1.9(1)
U(NR$_2$)$_6$$^-$	MO-RSO	6.2(2)	1.7(1)	0.13(4)	0.04(2)	2.042
	MO-T[c]	–	–	–	–	–
	CF	5.5(5)	1.9(2)	–	–	2.0(1)
U(NCR$_2$)$_6$$^-$	MO-RSO	6.4(2)	0.8(1)	0.12(3)	0.15(2)	2.042
	MO-T	6.1(3)	1.0(3)	0.20(8)	0.05(4)	1.81(6)
	CF	5.5(4)	1.4(2)	–	–	1.76(8)
UR$_6$$^-$	MO-RSO	6.8(4)	0.05(2)	0.0(8)	0.02(2)	2.042
	MO-T[c]	–	–	–	–	–
	CF	6.8(2)	0.00(9)	–	–	1.95(4)
NpF$_6$	MO-RSO	16.7(1)	5.20(7)	0.16(2)	0.044(6)	2.518
	MO-T	16.7(1)	5.1(1)	0.31(6)	0.06(3)	2.52(8)
	CF	16.1(8)	5.4(4)	–	–	2.4(2)

[a]Standard deviations given in parentheses and are in the same units as the last digit of the parameter. Values without parentheses were not allowed to vary in the fit. [b]ζ_f in the case of the MO-RSO fit. [c]Too few data available to apply the MO-T model.

Table 4. Covalency in the Bonding t_{1u} and t_{2u} Orbitals and Estimated Strengths of Bonds Formed between the Ligands and the f Orbitals[a]

complex	model	% f orbital $t_{1u}(\sigma,\pi)$	e^- density[b] $t_{2u}(\pi)$	σ bond (kcal mol^{-1})	π bond[c] (kcal mol^{-1})	avg M−X (kcal mol^{-1})
CeCl$_6$$^{3-}$	MO-RSO	0(4)	0(3)	0.7	0.2	1.1
$E_M = 6.73$	MO-T	0(17)	1(13)	0.6	0.2	1.1
$E_X = 12.97$	CF	–	–	0.6	0.2	1.1
PaCl$_6$$^{2-}$	MO-RSO	6(6)	3(4)	2.7	1.2	5.2
$E_M = 7.60$	MO-T	31(9)	20(2)	3.9	0.0	3.9
$E_X = 12.97$	CF	–	–	2.8	1.2	5.2
UF$_6$$^-$	MO-RSO	13(4)	4(1)	7.6	2.5	12.5
$E_M = 9.33$	MO-T	23(8)	6(4)	7.6	2.4	12.4
$E_X = 17.42$	CF	–	–	7.1	2.6	12.4
UCl$_6$$^-$	MO-RSO	18(4)	6(2)	8.5	2.1	12.6
$E_M = 9.33$	MO-T	32(13)	7(6)	8.5	1.8	12.2
$E_X = 12.97$	CF	–	–	7.3	2.5	12.4
UBr$_6$$^-$	MO-RSO	26(7)	9(3)	10.1	1.4	12.9
$E_M = 9.33$	MO-T	49(19)	11(4)	10.1	0.8	11.6
$E_X = 11.81$	CF	–	–	7.8	2.4	12.7
U(OR)$_6$$^-$	MO-RSO	14(8)	6(3)	9.9	4.1	18.0
$E_M = 9.33$	MO-T	20(17)	0(7)	9.6	4.4	18.4
$E_X = 13.02$	CF	–	–	9.1	4.4	18.0
U(NR$_2$)$_6$$^-$	MO-RSO	14(5)	4(2)	13.1	2.6	18.3
$E_M = 9.33$	MO-T[d]	–	–	–	–	–
$E_X = 11.46$	CF	–	–	11.8	5.8	17.7
U(NCR$_2$)$_6$$^-$	MO-RSO	17(4)	13(2)	12.9	1.2	15.2
$E_M = 9.33$	MO-T	19(9)	5(4)	12.4	1.5	15.5
$E_X = 11.46$	CF	–	–	11.4	4.3	15.8
UR$_6$$^-$	MO-RSO	5(45)	3(2)	17.4	0.0	17.4
$E_M = 9.33$	MO-T[d]	–	–	–	–	–
$E_X = 9.84$	CF	–	–	17.6	0.0	17.6
NpF$_6$	MO-RSO	16(3)	4.2(5)	20.9	4.6	30.2
$E_M = 10.87$	MO-T	26(3)	5.7(5)	20.9	4.5	30.0
$E_X = 17.42$	CF	–	–	20.4	4.8	30.0

[a]Average M−X is the contribution of only f orbital bonding to the bond strength. [b]Fraction of the electron density that resides on the metal f orbitals in the bonding orbitals; the standard deviation is given in parentheses. [c]Note that the strength of a π bond is doubled for U(NR$_2$)$_6$$^-$ and U(NCR$_2$)$_6$$^-$ since the complexes contain half of the 5f p−π donor interactions of the other complexes. [d]Too few data to apply the MO-T model.

Table 5. Ligand Character (%) in the Antibonding Orbitals of UF$_6$$^-$, PaCl$_6$$^{2-}$, and NpF$_6$

complex	orbital	MO-RSO	MO-T	$X\alpha$[21]	DSW[29,30,78]
UF$_6$$^-$	Γ_6	13.4	23.0	14.1	15.2
UF$_6$$^-$	Γ_8'	12.4	21.2	13.6	16.9
UF$_6$$^-$	Γ_7'	3.0	4.1	5.6	4.4
UF$_6$$^-$	Γ_8	5.6	8.4	11.9	9.7
UF$_6$$^-$	Γ_7	1.4	1.9	3.8	3.2
PaCl$_6$$^-$	Γ_6	4.7	30.9		10.3
PaCl$_6$$^-$	Γ_8'	2.7	29.0		8.5
PaCl$_6$$^-$	Γ_7'	0.1	10.0		6.3
PaCl$_6$$^-$	Γ_8	2.2	22.3		8.8
PaCl$_6$$^-$	Γ_7	0.0	11.9		2.7
NpF$_6$	Γ_7	1.2	1.7		0.9