X-ray \(L_{\mathrm{III}}\)-Absorption Spectra and the Nature of Bonding in Complex Compounds of \(\mathrm{Re}^{\mathrm{II}}\), \(\mathrm{Re}^{\mathrm{IV}}\), \(\mathrm{Re}^{\mathrm{VII}}\)

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Abstract

Full Text

Chemistry

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X-ray L_{III}-Absorption Spectra and the Nature of Bonding in Complex Compounds of Re^{II}, Re^{IV}, Re^{VII}

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The study of the fine structure of X-ray spectra makes it possible to judge the nature of the chemical bond and the charge of the central atom in coordination compounds ([1–5]). Thus, for example, in ([2]) an approximate method is given for calculating the charge of osmium atoms in complexes from the decomposition of the contour of the absorption curve into a series of lines and the true absorption edge. The development of the theory of short-range order in X-ray spectroscopy ([6, 7]) will probably make it possible to determine the effective charge of the central atom, the radius of the first coordination sphere, and the mean potential of an electron in the crystal lattice of solids.

In the present communication are given the results of an experimental study of the rhenium L_{III}-absorption spectra in different valence states: Re^{II}, Re^{IV}, Re^{VII}, and also of metallic rhenium. On the basis of an analysis of the absorption curves of rhenium in the metal, NH_4HReCl_4, $RePy_2Cl_4$, $(NH_4)_2ReCl_6$, and NH_4ReO_4, an attempt has been made to estimate the effective charge of rhenium in the vicinity of the 5*d*-shell, as well as the mean potential of the electron in the crystal lattice and the radius of the first coordination sphere on the basis of the theory of short-range order ([7]). The rhenium L_{III}-absorption spectra were obtained on a short-wavelength X-ray spectrograph with a bent quartz crystal $(10\bar{1}0)$ in the second order of reflection. The dispersion was 8.25 XU/mm, resolving power 10000. The absorbers were prepared by mixing finely ground powder with Canada balsam; the mixture was poured onto tissue paper. The surface density was 10–20 mg/cm^2. The X-ray source was a BSV tube with a molybdenum anode; tube voltage 15–20 kV, current 20 mA; registration was photographic, exposure 1–3 hours.

Fig. 1. Rhenium X-ray L_{III}-absorption spectra

The blackening curve was constructed for each photograph by the method of ([8]),

using the K_{α,α_2}- and K_{β_1,β_3}-lines of molybdenum. The blackening-distribution curves $S = S(l)$ were recalculated into distribution curves of the relative absorption coefficients $\mu|E| \sim -\lg I(l)$; the results were averaged over twelve

absorption curves obtained from three or four photographs over a length of 6 mm (300–400 eV) in the vicinity of the L_{III} absorption edge. In calculating the wavelengths, the nearest molybdenum lines were used as comparison lines.

The results of the measurements are given in Fig. 1 and in Table 1, where: ΔE is the shift of the white line of the compound toward higher energies relative to metallic rhenium; ΔE_i are the distances of the maxima (i even) and minima (i odd) of the fine structure of the L_{III}-absorption spectra from the inflection point on the long-wavelength side ($i = 1$).

Table 1

	Re_{met}	$NH_4HReCl_4RePy_2Cl_4$		$(NH_4)_2ReCl_6$	NH_4ReO_4
Coordination number	$12^{(14)}$	–	–	$6^{(11)}$	$4^{(12)}$
Interatomic Re—Re distances r, Å	2.7	–	–	–	–
Interatomic Re—Cl distances r, Å	–	–	–	–	–
Interatomic Re—O distances r, Å	–	–	–	–	1.87
Wavelength of the white line λ, XU	1174.24	1174.12	1174.08	1173.92	1173.98
Energy of the white line E, eV	10534.8	10535.8	10536.2	10537.7	10537.1

		Re_{met}	$NH_4HReCl_4RePy_2Cl_4$		$(NH_4)_2ReCl_6NH_4ReO_4$	
Shift of the white line ΔE, eV		0	+1	+1	+3	+2
Charge in the vicinity of $5d$		0	+0.5	+0.5	+1.5	+1.0
Position of fine-structure extrema ΔE_i, eV	$i = 1$	0	0	0	0	0
Position of fine-structure extrema ΔE_i, eV	2	6.3	3.6	4.8	5.6	4.8
Position of fine-structure extrema ΔE_i, eV	3	14	11	12	15	12
Position of fine-structure extrema ΔE_i, eV	4	20	18	18	18	16

		Re_{met}	$NH_4HReCl_4RePy_2Cl_4$		$(NH_4)_2ReCl_6NH_4ReO_4$	
Position of fine-structure extrema ΔE_i, eV	5	26	25	28	30	38
Position of fine-structure extrema ΔE_i, eV	6	34	49	50	54	74
Position of fine-structure extrema ΔE_i, eV	7	45	82	80	81	106
Position of fine-structure extrema ΔE_i, eV	8	73	112	113	110	167
Position of fine-structure extrema ΔE_i, eV	9	100	145	145	136	225
Position of fine-structure extrema ΔE_i, eV	10	123	189	188	177	302

		Re_{met}	$NH_4HReCl_4RePy_2Cl_4$		$(NH_4)_2ReCl_6NH_4ReO_4$
Position of fine-structure extrema ΔE_i, eV	11	150	231	234	221
Position of fine-structure extrema ΔE_i, eV	12	179	281	282	266
Position of fine-structure extrema ΔE_i, eV	13	220	336	333	329
Position of fine-structure extrema ΔE_i, eV	14	264	388	389	390
Position of fine-structure extrema ΔE_i, eV	15	301			
Position of fine-structure extrema ΔE_i, eV	16	360			

As can be seen from Fig. 1 and the data of Table 1, there is a shift of the white line ($i = 2$) of the rhenium L_{III}-absorption spectrum with a change in formal valence. In works [9,10] it was established for the rhenium L_{III}-absorption spectra in the metal, $ReO_2 \cdot 2H_2O$, K_2ReCl_6, and $KReO_4$ that the shift of the white line increases in proportion to the formal valence. In the case of the compounds we studied, $(NH_4)_2ReCl_6$ and $RePy_2Cl_4$, shifts of the white line by +3 eV and +1 eV, respectively, are observed, despite the fact that in both compounds rhenium is formally tetravalent. The Re^{IV} compounds considered differ in the character of the immediate environment of the central rhenium atom and, consequently, in the effective charge of rhenium.

If one takes into account that the physical meaning of charge consists in the degree to which electrons of the central atom are withdrawn by the atoms of the immediate environment, then the charge in the vicinity of the $5d$ shell can be estimated by interpolation from the shift of the white line, as was done in work [5] for calcium compounds. The charge values in the vicinity of the $5d$ shell obtained in this way are given in Table 1.

The smaller charge of the central rhenium atom in the vicinity of the $5d$ shell in NH_4ReO_4, compared with $(NH_4)_2ReCl_6$, suggests d^3s-hybridization in NH_4ReO_4, rather than sp^3-hybridization.

As is evident from the data of Table 1 and Fig. 1, the dependence of the short-wave structure of the rhenium L_{III}-absorption edge on the coordination number is quite clearly expressed, and consequently [14] also on the interatomic distance for metallic rhenium, $(NH_4)_2ReCl_6$, and NH_4ReO_4, whose structures are known [11,12,14]. This confirms the theory of short-range order [6]. On the basis of the similarity of the short-wave fine structure of $(NH_4)_2ReCl_6$ and $RePy_2Cl_4$ (Fig. 1), one may suppose that in $RePy_2Cl_4$ the coordination is also octahedral or close to octahedral.

On the basis of the experimental data obtained, an attempt was also made to determine the limits of applicability of the approximate formula [7] for the compounds considered with unknown structure. The conditions for maxima of the relative absorption coefficient under scattering of $2p$-electrons ejected from the absorbing atom by atoms of the first coordination sphere are written as:

$$2k_m r_1 + 2\eta_2(k_m) = \frac{\pi}{2} + 2m\pi. \tag{1}$$

Here: r_1 is the radius of the first coordination sphere,

$$k_m = \frac{\sqrt{2m}}{\hbar} \cdot \sqrt{\Delta E_m + A},$$

ΔE_m are the distances of the maxima of the fine structure from the inflection point on the long-wave side ($m \neq i$), $A = U_0 - \varphi$, U_0 is the mean potential of

the electron in the lattice, φ is the electron work function, and η_2 is the atomic scattering phase of the $2p$-electron.

If it is assumed that, in some interval of values of k_m, the scattering phase η_2 is constant, then for three neighboring maxima of the fine structure with energies ΔE_m, ΔE_{m+1}, and ΔE_{m+2}, the three conditions (1) are satisfied simultaneously if there exists a real solution of the equation:

$$f(A) = \sqrt{\Delta E_m + A} - 2\sqrt{\Delta E_{m+1} + A} + \sqrt{\Delta E_{m+2} + A} = 0. \qquad (2)$$

By substituting successively different values of A from 5 to 40 eV for various sets of three neighboring experimental values ΔE_i, it was found that for metallic rhenium at $A = 17.5$ eV equation (2) is valid for all sets beginning with the set 34, 74, 123 eV (see Table 1); consequently, these maxima of the fine structure of the L_{III}-absorption edge are due to scattering of the $2p$-electron ejected upon absorption by atoms of the first coordination sphere. The radius of the first coordination sphere can be estimated from the formula:

$$r_1 = \frac{6.15 \cdot 10^{-8}}{\sqrt{\Delta E_{m+1} + A} - \sqrt{\Delta E_m + A}}, \qquad (3)$$

whence for metallic rhenium one obtains $r_1 = 2.7$ Å. This agrees with data on interatomic distances in metallic rhenium [14]. In the case of NH_4HReCl_4 and $RePy_2Cl_4$, only for one set, 112, 189, 281 eV, was such a value of A found ($A = 27.5$ eV) for which condition (2) is satisfied; in this case formula (3) gave $r_1 = 2.2$ Å.

For the compounds $(NH_4)_2ReCl_6$ and NH_4ReO_4, no set of ΔE_i was found for which condition (2) would be satisfied in the indicated interval of values of A. This is apparently due to the presence of a periodic field of the ionic environment in these compounds.

Thus, the approximate theory of the fine structure of x-ray absorption spectra [7] proved applicable for calculating certain parameters not only of metallic rhenium, but also of the coordination compounds NH_4HReCl_4 and $RePy_2Cl_4$. This is apparently associated with the covalent character of the rhenium bonds in these compounds, as well as with the presence of Re—Re bonds in NH_4HReCl_4, whose structure is probably analogous to the structure of $(PyH)HReCl_4$ [13].

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Note: Figure translations are in progress. See original paper for figures.