

## Interpretation of the Quadrupole Splitting Parameters in the Mossbauer Spectra of Ruthenium(III) Complexes

DAVID C. FOYT, T. H. SIDDALL, III, C. J. ALEXANDER, and M. L. GOOD\*

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The  $^{99}\text{Ru}$  Mossbauer spectra of Ru(III) complexes exhibit a considerable range of values for the quadrupole splitting, including zero, whereas a nonzero splitting is consistently observed in the corresponding low-spin Fe(III) compounds. These results are interpreted in terms of a crystal field model in the strong field limit, where the  $t_{2g}^5$  configuration can be treated as an equivalent one-electron problem. The quadrupole splitting vanishes in a field of pure octahedral symmetry and increases as the ratio of the axial distortion to the spin-orbit coupling increases. The absence of observable splitting for many Ru(III) complexes is due to their high degree of symmetry, together with the larger spin-orbit coupling and the smaller value of  $Q\langle r^{-3} \rangle_0$ , as compared to low-spin Fe(III) complexes.

### Introduction

Recent studies of the Mossbauer effect in ruthenium complexes have demonstrated that the Mossbauer parameters can be correlated with chemical properties in a variety of situations. Although brief consideration has been given to the quadrupole splitting,<sup>1</sup> previous work has dealt primarily with the isomer shift. In the present study we investigate the relationship between the quadrupole splitting ( $\Delta E_Q$ ) and the structure of a number of Ru(III) low-spin  $d^5$  complexes. These compounds are of particular interest because they exhibit a considerable range of quadrupole splittings, from essentially zero to 0.85 mm/sec. It is a commonly used rule of thumb in iron Mossbauer spectroscopy that the valence contribution to the nucleus vanishes due to symmetry in the case of filled or half-filled octahedral orbital shells and is generally nonzero otherwise. In fact, however, the quadrupole splitting is predicted to vanish identically for all systems of pure octahedral symmetry, regardless of the formal electronic configuration.<sup>2,3</sup> Although this fact is generally recognized, most authors neglect to discuss its theoretical and structural implications in terms of the observed values of the quadrupole splitting parameters. In general, the magnitude of the splitting in Ru(III) complexes correlates with distortion from octahedral symmetry in the same way as in the formally analogous Fe(III) complexes, although examples of singlet spectra among the latter are much less common. We discuss the correlation with distortion in these two systems in terms of an effective crystal field model. Figure 1 shows the splitting of the  $T_{2g}$  electronic ground state under the influence of axial distortion

and spin-orbit interaction. The corresponding ground state wave function is employed to evaluate  $\Delta E_Q$  at 4.2°K for each system.

### Experimental Section

The Mossbauer parameters obtained in our laboratory for a number of Ru(III) complexes are given in Table I together with parameters for previously reported Ru(III) complexes. Parameters for several low-spin Fe(III) complexes are given in Table II for comparison.<sup>1,4,5</sup> The isomer shifts of Table I are typical for Ru(III).<sup>5</sup> Representative spectra are displayed in Figure 2. The errors indicated for the isomer shift and quadrupole splitting values are calculated from the error analysis of the least-squares Lorentzian fit to the data. For all data taken in our laboratory, the isomer shift and quadrupole splitting values were reproducible (comparison of two or more spectra) to within  $\pm 0.05$  and  $\pm 0.05$  mm/sec, respectively. The Mossbauer spectra were obtained with the apparatus previously described.<sup>6</sup> The use of a germanium-lithium drifted detector (Elscont Ltd. Model GP/GC) resulted in improved resolution over that previously reported. A Kontes/Martin glass dewar system was employed, and both source and absorber were immersed directly in the liquid helium well.

In the absence of a resolved quadrupole splitting it is customary to take the full width at half maximum as a measure of the splitting. This procedure is not always reliable, however, because of broadening due to sample thickness, nonrigidity of the lattice, and other factors. Such considerations are especially important in the case of low per cent effect. Unfortunately, the per cent effect has not usually been reported for these compounds.

Since  $\Delta E_Q$  is expected to correlate with the degree of distortion from octahedral symmetry, we have also studied the far-infrared spectra of several of these complexes, especially those which are believed to be of very nearly pure octahedral symmetry. The spectra of  $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{RuCl}_6]$  and  $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{RuBr}_6]$  are shown in Figure 3. The vibrational peaks  $\nu_3$  and  $\nu_4$  are observed in both complexes, although the shape of the  $\nu_3$  peak for the chloride complex is obscured by the proximity of a peak due to the cation. The symmetric shape of  $\nu_4$ , and of both  $\nu_3$  and  $\nu_4$  for the bromide complex, implies that the Ru(III) ion is in an essentially octahedral

(1) C. A. Clausen, III, R. A. Prados, and M. L. Good, *Chem. Phys. Lett.*, **8**, 565 (1971).

(2) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961, pp 159-166.

(3) The absence of a valence contribution to  $\Delta E_Q$  from filled and half-filled shells is to be explained by the fact that axial distortion does not produce a quadrupole splitting in these systems, whereas it does so for other configurations, such as  $t_{2g}^5$ . A more detailed theoretical analysis of this problem has been given elsewhere: D. C. Foyt, *Inorg. Nucl. Chem. Lett.*, submitted for publication.

(4) G. Kaindl, W. Potzel, F. Wagner, U. Zahn, and R. L. Mossbauer, *Z. Phys.* **226**, 103 (1969).

(5) W. Potzel, F. Wagner, U. Zahn, R. L. Mossbauer, and J. Danon, *Z. Phys.*, **240**, 306 (1970).

(6) C. A. Clausen, III, R. A. Prados, and M. L. Good, *Mossbauer Eff. Methodol., Proc. Symp.*, **6**, 31 (1971).

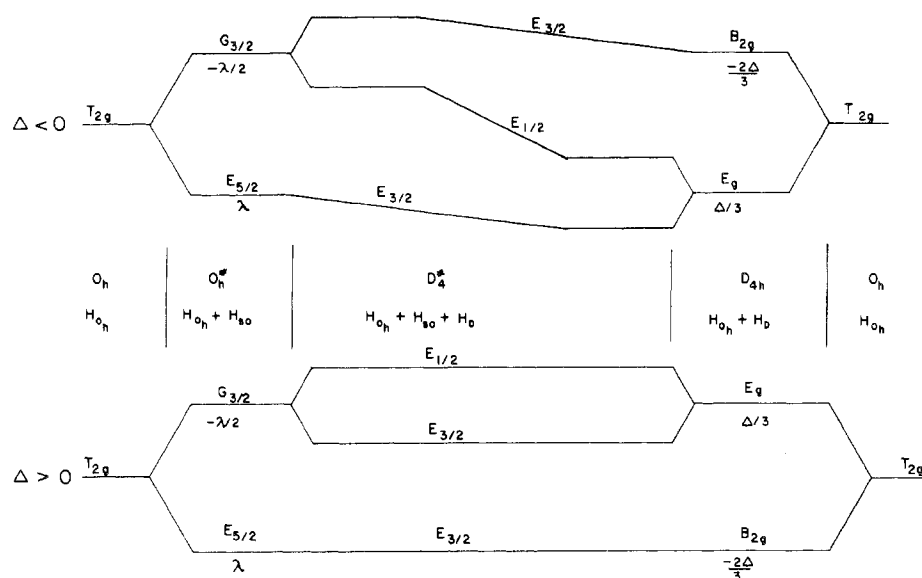


Figure 1. Energy level diagram for the  $t_{2g}^5$  configuration with axial distortion and spin-orbit interaction.

Table I. Mossbauer Parameters for Ru(III) Complexes

	Compd	Isomer shift, mm/sec	$\Delta E_Q$ , mm/sec	Fwhm, mm/sec	Ref
I	$K_3[RuF_6]$	$-0.84 \pm 0.01$		0.48	<i>d</i>
II	$[N(CH_2CH_2NH_3)_3][RuCl_6]$	$-0.70 \pm 0.02$		0.32	<i>a</i>
III	$[N(CH_2CH_2NH_3)_3][RuBr_6]$	$-0.79 \pm 0.02$		0.36	<i>a</i>
IV	$[Ru(NH_3)_6]Cl_3$	$-0.49 \pm 0.01$		0.52	<i>c</i>
V	$[Ru(NH_3)_6]Br_3$	$-0.50 \pm 0.06$		0.74	<i>d</i>
VI	$[Ru(bipy)_3](ClO_4)_3$	$-0.54 \pm 0.01$		0.28	<i>c</i>
VII	$[Ru(NH_3)_5Br]Br_2$	$-0.53 \pm 0.02$		0.60	<i>d</i>
VIII	$[Ru(NH_3)_4(OH)Cl]Cl \cdot 2H_2O$	$-0.39 \pm 0.01$		0.66	<i>c</i>
IX	$K_2[RuCl_5(H_2O)]$	$-0.71 \pm 0.02$	$0.32 \pm 0.02$	0.34	<i>d</i>
X	$[Ru(NH_3)_5Cl]Cl_2$	$-0.53 \pm 0.01$	$0.38 \pm 0.01$	0.34	<i>c</i>
XI	$[Ru(NH_3)_5(H_2O)](NO_3)_3$	$-0.50 \pm 0.07$	$0.49 \pm 0.05$	0.64	<i>d</i>
XII	$(Bu_4N)_3[Ru(SCN)_6]$	$-0.49 \pm 0.04$	$0.53 \pm 0.05$	0.44	<i>c</i>
XIII	$[Ru(NH_3)_4Cl_2]I_2$	$-0.56 \pm 0.02$	$0.57 \pm 0.02$	0.34	<i>d</i>
XIV	$[Ru(NH_3)_4Cl_2]Cl \cdot H_2O$	$-0.51 \pm 0.01$	$0.58 \pm 0.01$	0.30	<i>d</i>
XV	$\beta$ - $RuI_3$	$-0.81 \pm 0.08$	$0.58 \pm 0.08$	0.33	<i>b</i>
XVI	$\beta$ - $RuBr_3$	$-0.75 \pm 0.02$	$0.65 \pm 0.03$	0.46	<i>c</i>
XVII	$\beta$ - $RuCl_3$	$-0.67 \pm 0.05$	$0.79 \pm 0.05$	0.35	<i>b</i>

<sup>a</sup> Present work. Compounds prepared as outlined by J. R. Gaylor and C. V. Senoff, *Inorg. Chem.*, **11**, 2551 (1972). <sup>b</sup> C. A. Clausen, III, R. A. Prados, and M. L. Good, *Chem. Phys. Lett.*, **8**, 565 (1971). <sup>c</sup> G. Kaindl, W. Potzel, F. Wagner, U. Zahn, and R. L. Mossbauer, *Z. Phys.*, **226**, 103 (1969). <sup>d</sup> W. Potzel, F. Wagner, U. Zahn, R. L. Mossbauer, and J. Danon, *ibid.*, **240**, 306 (1970).

environment. This fact is further supported by the X-ray structure of  $[(C_6H_5N)_3][RuBr_6] \cdot 3C_6H_5NBr$  in which all of the Ru-Br bond lengths are equal and all of the Br-Ru-Br angles are found to be  $90^\circ$  within experimental error.<sup>7</sup>

The highly symmetrical complexes discussed above have singlet Mossbauer spectra. On the other hand, the  $\beta$ -ruthenium trihalides, whose X-ray structures indicate a high degree of distortion, and whose magnetic behavior implies considerable metal-metal interaction,<sup>8-10</sup> exhibit large quadrupole splittings. Direct comparison with corresponding Fe(III) compounds is not possible, since the Fe(III) halides are high-spin complexes. Nevertheless, it is of interest that very few low-spin Fe(III) complexes have singlet Mossbauer spectra<sup>11</sup> (see Table II), while singlets are common for Ru(III).

### Theory

In order to compare the quadrupole splittings in Ru(III) and Fe(III) complexes, and to rationalize the former more quantitatively in terms of distortion from cubic symmetry,

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(8) J. M. Fletcher, W. E. Gardner, A. C. Fox, and G. Topping, *J. Chem. Soc. A*, 1038 (1967).

(9) M. M. Crozat and S. F. Watkins, *J. Chem. Soc., Dalton Trans.*, 2512 (1972).

(10) Von K. Brodersen, H.-K. Breitbach, and G. Thiele, *Z. Anorg. Allg. Chem.*, **357**, 162 (1968).

(11) E. Fluck and P. Kuhn, *Z. Anorg. Allg. Chem.*, **350**, 263 (1967).

we employ crystal field theory to calculate  $\Delta E_Q$  in terms of the distortion and spin-orbit coupling parameters. The nuclear problem is essentially the same in both cases, the quadrupole splitting being due to the splitting of the  $I = 3/2$  nuclear excited state, brought about by the interaction between the quadrupole moment of the nucleus and the electric field gradient (EFG) at the nucleus. The splitting is

$$\Delta E_Q = \frac{eQV_{zz}}{2} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}$$

where  $V_{zz}$  and  $\eta = (V_{xx} - V_{yy})/V_{zz}$  are given in terms of the principal axis system. The small splitting of the  $I = 5/2$  ground state of the ruthenium nucleus serves only to broaden the doublet spectrum and, in the case of small  $\eta$ , to introduce a slight asymmetry of the two peaks (*i.e.*, their shapes, but not their relative areas, may be altered, see ref 12).

The values of  $V_{zz}$  and  $\eta$  depend both on the deviation of the electronic wave function from spherical symmetry

(12) Our neglect here of asymmetric broadening in Ru(III) spectra due to the ground state splitting is compensated by its neglect in the calculation of the quadrupole moment for <sup>99</sup>Ru. Check further ref 17 and D. C. Foyt, J. G. Cosgrove, R. L. Collins, and M. L. Good, *J. Inorg. Nucl. Chem.*, submitted for publication.

Table II. Mossbauer Parameters for Low-Spin Fe(III) Compounds

Compd	T, °K	Isomer shift, mm/sec <sup>h</sup>	$\Delta E_Q$ , mm/sec	Ref
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	298	-0.124	0.28	a
	77		0.47	
	4.2		0.52	
Cs <sub>3</sub> [Fe(CN) <sub>6</sub> ]	300	-0.14	0.36	b
	80	-0.04	0.47	
Na(Me <sub>4</sub> N) <sub>2</sub> [Fe(N <sub>3</sub> ) <sub>6</sub> ]	298	-0.074		c
	163	-0.154		
Na(Me <sub>4</sub> N) <sub>2</sub> [Fe(CN) <sub>6</sub> ]	163	i		c
Na <sub>2</sub> [Fe(CN) <sub>5</sub> (NO <sub>2</sub> )]	298	-0.09	1.78	d
[Fe(en) <sub>3</sub> ]Cl <sub>3</sub>	298	+0.14	1.09	e
[Fe(phen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	300	+0.05	1.62	f
	80	+0.10	1.71	
[Fe(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	300	+0.03	1.69	f
	80	+0.06	1.80	
[Fe(terpy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	298	-0.01	3.09	g
	77	+0.07	3.43	

<sup>a</sup> W. T. Oosterhuis, G. Lang, and S. DeBenedetti, *Phys. Lett. A*, **24**, 346 (1967). <sup>b</sup> B. V. Borshagovskii, V. I. Goldanskii, G. B. Seifer, and R. A. Stukan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1716 (1968). <sup>c</sup> E. Fluck and P. Kuhn, *Z. Anorg. Chem.*, **350**, 263 (1967). <sup>d</sup> J. Danon, *J. Chem. Phys.*, **41**, 3378 (1964). <sup>e</sup> G. A. Renovitch and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, **90**, 3585 (1968). <sup>f</sup> R. R. Berrett, B. W. Fitzsimmons, and A. Owusu, *J. Chem. Soc. A*, 1575 (1968). <sup>g</sup> W. M. Reiff, W. A. Baker, Jr., and N. E. Erickson, *J. Amer. Chem. Soc.*, **90**, 4794 (1968). <sup>h</sup> With respect to Fe metal. <sup>i</sup> The isomer shift has not been reported, although the absence of quadrupole splitting has been noted in footnote c.

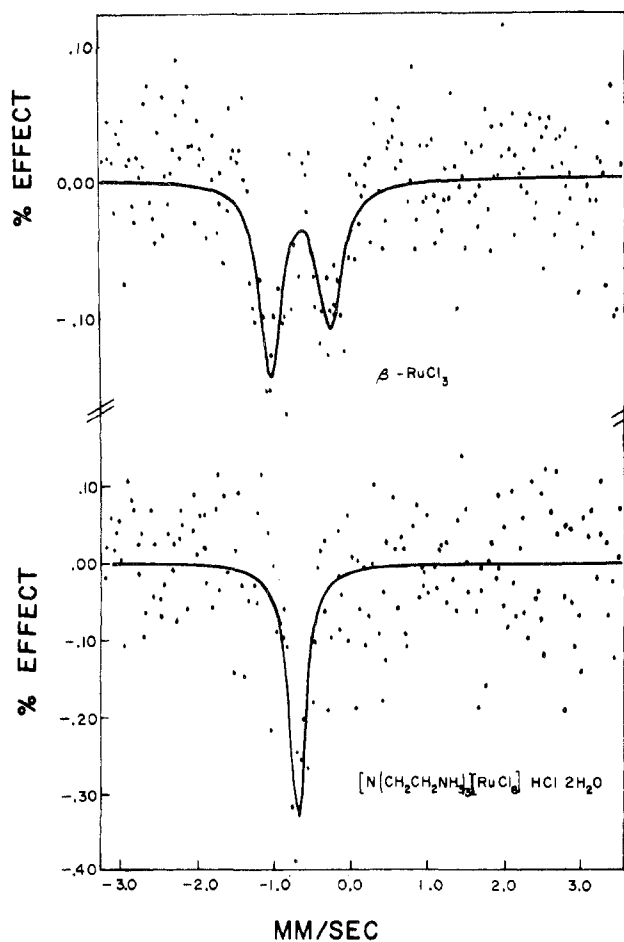


Figure 2. <sup>99</sup>Ru Mossbauer spectra for [N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>3</sub>][RuCl<sub>6</sub>] and β-RuCl<sub>3</sub>.

(valence contribution) and on the lattice distortion. For partially filled shells the former tends to predominate, and we will neglect the lattice contribution. For the valence con-

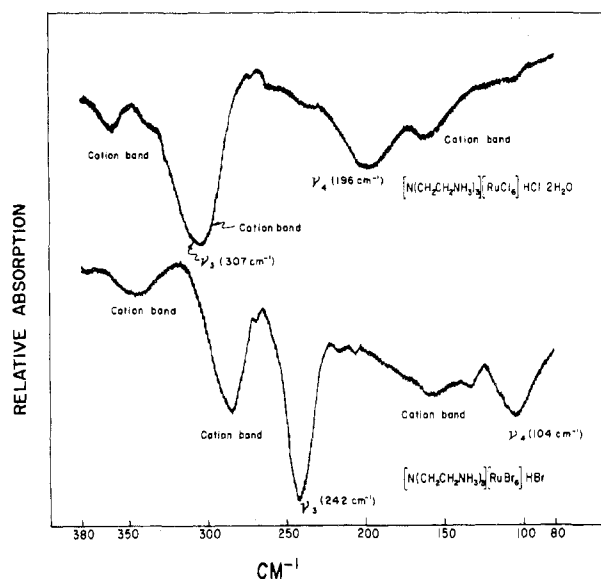


Figure 3. Far-infrared spectra for [N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>3</sub>][RuCl<sub>6</sub>] and [N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>3</sub>][RuBr<sub>6</sub>]. (The ν<sub>3</sub> peak positions check with those reported by J. R. Gaylor and C. V. Senoff in *Inorg. Chem.*, **11**, 2551 (1972).)

tribution, the low-spin d<sup>5</sup> configuration can be treated as a pure t<sub>2g</sub><sup>5</sup> configuration, neglecting interaction with other octahedral orbital configurations. By the hole theorem, this is equivalent to a t<sub>2g</sub><sup>1</sup> configuration with the signs of the distortion and spin-orbit coupling parameters reversed. Here we consider only axial distortion, whether tetragonal or trigonal. The energies and wave functions for the appropriate Hamiltonian

$$\mathcal{H} = \lambda \mathbf{l} \cdot \mathbf{s} - \frac{\Delta}{3} (l_z^2 - 2)$$

on the space

$$V(t_{2g}): \{ |t_{2g}; i\rangle | \sigma \rangle, i = 1 \text{ to } 3, \sigma = \alpha, \beta \}$$

have been previously reported.<sup>13,14</sup> The spin-orbit coupling parameter λ is taken to be negative, in accordance with the hole theorem. The values of V<sub>zz</sub> and V<sub>xx</sub> - V<sub>yy</sub> are given by the expectation values of the operators<sup>15</sup>

$$V_{zz} = -\frac{2e}{r^3} \left( \frac{4\pi}{5} \right)^{1/2} Y_2^0$$

and

$$V_{xx} - V_{yy} = \frac{-3e}{r^3} \left( \frac{8\pi}{15} \right)^{1/2} (Y_2^2 + Y_2^{-2})$$

The second of these vanishes in axial symmetry, and the quadrupole splitting due to the *j*th electronic state is

$$(\Delta E_Q)_j = \frac{2}{7} e^2 Q \langle r^{-3} \rangle s_j$$

where s<sub>j</sub> is known in terms of the eigenvector coefficients.<sup>13</sup>

Since ruthenium Mossbauer spectra are obtained at liquid helium temperature, only the contribution from the lowest electronic state is required. Figure 4 shows |s<sub>1</sub>| as a function of |Δ/λ| for a positive and negative Δ. The vanishing of s<sub>1</sub>

(13) R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).

(14) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).

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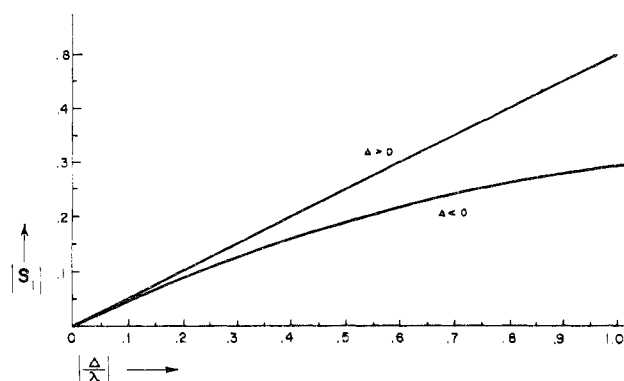


Figure 4. Relative contribution to  $\Delta E_Q$  from the lowest electronic state.

(and in general of  $V_{zz}$  and  $\eta$ ) in pure cubic symmetry is expected on group-theoretical grounds.<sup>3</sup>

In order to compare  $\Delta E_Q$  in Fe(III) and Ru(III), we require values for  $e^2Q\langle r^{-3} \rangle$  in each case. The accepted value for iron<sup>16</sup> is 14 mm/sec. For ruthenium we employ the value<sup>17</sup>  $0.34 \pm 0.07 \times 10^{-28}$  m<sup>2</sup> for the quadrupole moment, together with the free ion value<sup>18</sup> 7.1 au for  $\langle r^{-3} \rangle$ , obtained by extrapolation from Hartree-Fock calculations.<sup>19</sup> Then  $e^2Q\langle r^{-3} \rangle = 6.5$  mm/sec.<sup>20</sup> Assuming that a splitting of 0.1 mm/sec is the smallest that can be resolved in each case, we find that  $|S_1|$  must be greater than 0.025 for Fe or 0.054 for Ru. From Figure 4, we obtain lower limits of 0.06 and 0.13 for  $|\Delta/\lambda|$  (or slightly less if  $\Delta > 0$ ). Finally, taking typical values<sup>21</sup> of  $-450$  and  $-1000$  for  $\lambda$  in Fe, Ru, we obtain lower limits of 27 and 130 cm<sup>-1</sup> for  $|\Delta|$  in the two cases.

### Discussion

We have computed approximate lower bounds for the axial distortion parameter  $|\Delta|$ , in the presence of observable quadrupole splitting, for complexes of low-spin Fe(III) and Ru(III). It is found that the distortion parameter in the Ru(III) complexes must be approximately five times as large as is required in the Fe(III) complexes, in order for valence contributions to  $\Delta E_Q$  to be observed. This is due both to the larger spin-orbit interaction in Ru and to the smaller value of  $Q\langle r^{-3} \rangle$  for the excited ( $S = 3/2$ ) state in <sup>99</sup>Ru. Furthermore, second row transition metal complexes are expected to deviate more from the crystal field model which will result in lower values for the "orbital reduction factor." Thus it is expected that complexes of Ru(III) having nearly pure octahedral symmetry may have singlet Mossbauer spectra, in agreement with observation. On the other hand, the spectra of low-spin Fe(III) complexes will more frequently show a quadrupole splitting.

The numerical results obtained above provide only a semi-quantitative estimate of the relative distortion required in the two species in order to produce an observable quadrupole splitting. They should not be applied to the quantitative determination of  $\Delta$ , due to the neglect of the orbital reduc-

tion factor, the Sternheimer screening factor, the lattice contribution to  $\Delta E_Q$ , and to the prior choice of a fixed value for  $\lambda$ .<sup>12</sup> A more precise treatment of the problem requires fitting  $\Delta E_Q$  as a function of temperature,<sup>13,16</sup> which is precluded for <sup>99</sup>Ru by the low recoil-free fraction. Moreover, even if  $\Delta$  were known, the correlation between  $\Delta$  and the details of the physical structure is far from straightforward.<sup>22</sup>

The above analysis does yield useful qualitative information, however, about several of the compounds in Table I. It is already known from X-ray structural analysis, far-ir spectra, and magnetic susceptibility data that the hexahalides of Ru(III) (I-III of Table I) are essentially octahedral in structure and that the  $\beta$ -trihalides (XV-XVII) are highly distorted. The quadrupole splittings show the expected correlation with distortion in these compounds.

The structure of the thiocyanate complex (XII) has been the subject of considerable discussion.<sup>23</sup> In the Ahrland-Chatte-Davies-Pearson classification scheme, Ru(III) is nominally classified as "soft,"<sup>24</sup> which implies S bonding in the present system, although its classification is actually a borderline case.<sup>25</sup> The infrared spectrum has features characteristic of both N and S bonding, and a bridged complex has been ruled out on the basis of other data.<sup>23</sup> The relatively large quadrupole splitting of the Mossbauer spectrum indicates that the structure is considerably distorted. This lends support to the view that the complex is mixed, with each site containing both N-bonded and S-bonded ligands. Of course, no final decision as to the structure can be made on the basis of these data alone.

The absence of quadrupole splitting in the Mossbauer spectrum of the bipyridyl complex (VI) indicates that its distortion from octahedral symmetry is relatively small. This conclusion is especially convincing in view of the narrow line width, which is essentially as small as the natural minimum for the 90-keV transition and is in striking contrast to the splitting of 1.76 mm/sec observed for  $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$ .<sup>26</sup> DeSimone and Drago<sup>27</sup> have reported epr results for the  $[\text{Ru}(\text{bipy})_3]^{3+}$  cation which they interpret in terms of a large distortion from octahedral symmetry ( $\Delta = -2000$ ). However, they point out that this solution may not be the correct one. Thus, the  $g$  values they report are not necessarily inconsistent with the results reported here.

The absence of observed splittings for compounds VII and VIII of Table I may be explained by the unusually large line widths, which are probably associated with low per cent effects and poorly resolved spectra. Such results are not unusual in ruthenium Mossbauer spectroscopy, and the anomalously large line width in compound V may be due to the same effect.

**Acknowledgments.** The authors are grateful to the National Science Foundation (Grant No. GP-9490 and GP-28113) for financial support.

**Registry No.**  $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)_3][\text{RuCl}_6]$ , 51472-17-4;  $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)_3][\text{RuBr}_6]$ , 51472-18-5; Ru(III), 22541-88-4; <sup>99</sup>Ru, 15411-62-8.

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(20) The Sternheimer screening factor has been neglected here. If the value of  $(1 - R)$  for Ru is significantly smaller than the approximate value of 0.68 for Fe, a large error will have been introduced into the numerical calculations.

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