Study of the Mössbauer Effect in Europium(III) Complexes

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^{151}Eu Mössbauer spectra of a number of europium(III) complexes, including aminopolycarboxylates, β-diketones, and 1,10-phenanthroline complexes, have been investigated. Isomer shifts of these complexes fall within a remarkably small range, indicating that their bonding is predominantly ionic in character, with the possibility of a small covalent contribution.

THE application of Mössbauer spectroscopy to the study of structure and bonding of lanthanide compounds is of interest.[1,2] In particular, solid compounds of europium can be investigated by means of ^{151}Eu Mössbauer spectroscopy. The isomer shift, with its dependence on the electron density at the nucleus, can yield information on the type of bonding found in europium compounds. Some of the earlier interpretations of the measured isomer shifts of Eu^{III} compounds were based on reports by Hüfner *et al.*[3,4] that the ^{151}Eu isomer shift of Eu_2O_3 relative to EuF_3 was less than 0·05 mm s^{-1}. However, recent investigations[5,6] have shown that the isomer shift of Eu_2O_3 (in the form commercially available) relative to $EuF_3,2H_2O$ is 1·06 ± 0·01 mm s^{-1}. There is therefore a need for further information on isomer shift values of Eu^{III} compounds. Mackey and Greenwood[7] have interpreted studies of the magnitude of the resonant effects in Eu^{III} chelates as an indication of the presence of polymerisation in Eu^{III} aminopolycarboxylate chelates.

EXPERIMENTAL

Preparation of Complexes.—A series of europium(III) chelates of the general formula $M[EuL]_x,yH_2O$, where M is a cation and L a multidentate aminopolycarboxylate ligand were prepared as described by Moeller *et al.*[8] Compounds were prepared with *N'*-(2-hydroxyethyl)ethylenediamine-*NNN'*-triacetic acid (hedta), ethylenediamine-*NNN'N'*-tetra-acetic acid (edta), 1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid (dcta), and diethylenetriamine-*NNN'N'N''*-penta-acetic acid (dtpa) as ligands, and H^+, K^+, NH_4^+, or Ba^{2+} as cations. A number of preparative methods[9–11] for europium(III) β-diketone complexes were attempted and found to give uncharacterisable products. The methods described by Melby *et al.*[12] and Bauer *et al.*[13] were used as a basis for the preparation of Eu^{III} β-diketone complexes. Complexes of the general formula, L[Eu(β-diketone)$_4$] where L is a cation (Na^+, K^+, $(C_2H_5)_4N^+$) were prepared by mixing together stoicheiometric amounts of europic chloride, the β-diketone, and a suitable base in an ethanolic medium.[12] The preparation and isolation of solid Eu^{III} tris-β-diketones proved more difficult and no general method was evolved. A series of Eu^{III} (1,10-phenanthroline)(β-diketone) compounds were prepared by the method of Bauer *et al.*[13] Other 1,10-phenanthroline complexes of Eu^{III} were prepared as described by Hart *et al.*[14] and Sinha *et al.*[15] Oxalato-complexes,[16,17]

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a picolinato-complex,[12] and a tropolonato-complex[18] were also prepared.

It has been pointed out by Dulaney and Clifford[5] and Turner[19] that in most of the previous ^{151}Eu Mössbauer studies careful sample characterization has been neglected. It is essential that the exact chemical nature of every sample should be determined. Analytical data for all the Eu^{III} complexes studied in the present investigation are in Table 1. The europium content was determined by weighing the ash (Eu_2O_3) remaining after combustion, and is subject to an uncertainty of the order of ±2%.

TABLE 1

Analytical data for europium complexes

Formula	C (%)		H (%)		N (%)		Eu (%)	
	Calc	Found	Calc	Found	Calc	Found	Calc	Found
Eu(hedta), $4·5H_2O$	23·62	23·65	4·72	4·75	5·5	5·5	30·0	34·4
H[Eu(edta)], $2·5H_2O$	24·7	25·2	3·70	3·8	5·8	6·0	31·3	32·5
NH_4[Eu(edta)],$2H_2O$	24·3	24·1	4·05	4·2	8·5	8·5	30·8	33·9
K[Eu(edta)],$4H_2O$	21·78	22·15	3·63	3·8	5·08	5·45		
Ba[Eu(edta)]$_2$,$7H_2O$	21·00	21·15	3·32	3·4	4·9	5·0		
H[Eu(dcta)],$4H_2O$	29·63	30·75	4·76	4·85	4·9	5·1	26·8	29·7
NH_4[Eu(dcta)],$5H_2O$	27·90	30·3	5·3	5·0	7·0	7·2	25·2	28·2
K[Eu(dcta)],$4H_2O$	27·80	28·65	4·30	4·45	4·63	4·65		
Ba[Eu(dcta)]$_2$,$11H_2O$	25·40	25·05	4·40	4·3	4·2	4·2		
$(NH_4)_2$[Eu(dtpa)],$2H_2O$	27·45	27·35	4·9	4·9	11·4	11·7	24·9	29·3
Ba[Eu(dtpa)],$7·5H_2O$	20·7	20·1	4·1	4·0	5·17	5·35		
Eu(AcCHAc)$_3$,$3H_2O$	36·0	36·2	5·4	5·3			30·2	30·4
Eu(tta)$_3$,H_2O	33·6	33·6	1·7	1·8				
(pip)[Eu(BzCHAc)$_4$]	61·3	61·0	5·3	5·35	1·60	1·65		
Na[Eu(BzCHAc)$_4$]	58·6	58·5	4·4	4·7				
K[Eu(BzCHAc)$_4$]	57·5	57·5	4·4	4·5				
(py)[Eu(CF_3·CO·CH·CO·CF_3)$_4$]	28·3	29·6	0·94	0·9			14·3	14·1
$(C_2H_5)_4N$[Eu(CF_3·CO·CH·CO·CF_3)$_4$]	30·3	30·1	2·2	2·1	1·3	1·3		
Me_4N[Eu(CF_3·CO·CH·CO·CF_3)$_4$]	27·4	27·0	1·5	1·5	1·3	1·2		
(isoq)[Eu(tta)$_4$]	42·2	42·2	2·1	2·1	1·2	1·35		
Eu(phen)(BzCH·CO·CF_3)$_3$	51·5	51·2	2·6	2·6	2·9	3·1		
Eu(phen)(tta)$_3$	43·4	43·5	2·0	2·0	2·9	3·1		
Eu(phen)$_3$(CNS)$_3$	54·0	53·0	2·7	2·7	14·5	13·4		
Eu(phen)$_2$$Cl_3$,$2H_2O$	44·0	43·5	3·1	3·2			23·2	22·1
Eu(phen)$_2$(benzoate)$_3$	61·7	61·3	3·5	3·65	6·4	6·35	17·4	16·9
Eu(phen)$_2$(*p*-hydroxybenzoate)$_3$	58·5	57·1	3·4	3·7			16·5	15·0
Eu(phen)$_2$(salicylate)$_3$	58·5	59·3	3·35	3·5	6·1	6·0	16·4	16·1
$Eu_2(C_2O_4)_3$,$10H_2O$	9·6	9·7	2·7	2·6			40·6	40·8
$Eu_2(CH_2·C_2O_4)_3$,$5H_2O$	15·4	15·6	2·3	2·8			43·0	42·0
$Eu_2([CH_2]_2·C_2O_4)_3$,$5H_2O$	19·4	20·0	2·96	2·95			41·0	42·0
$Eu_2([CH_2]_3·C_2O_4)_3$,$5H_2O$	23·0	23·9	3·57	2·65			38·8	36·1
Eu(picNO)$_3$$Cl_3$	37·0	36·6	3·6	4·0	7·2	7·2	26·0	26·3
Eu(tropolonate)$_3$	48·8	47·7	2·9	3·0			29·5	31·0

hedta = *N*′-(2-hydroxyethyl)ethylenediamine-*NNN*′-triacetate. edta = Ethylenediamine-*NNN*′*N*′-tetra-acetate. dcta = 1,2-diaminocyclohexane-NNN′N′-tetra-acetate. dtpa = Diethylenetriamine-*NNN*′*N*′*N*″-penta-acetate. phen = 1,10-Phenanthroline. tta = 2-Thenoyltrifluoroacetonate. picNO = 4-Picoline *N*-oxide. pip = Piperidinium. py = Pyridinium. isoq = Isoquinolinium.

The Mössbauer Spectrometer used is based on that described by Cranshaw[20] and was calibrated by means of a standard sodium nitroprusside absorber and a source of ^{57}Co in palladium. A Si(Li) diode was used for the detection of the 21·7 keV ^{151}Eu γ-ray from a $^{151}SmF_3,2H_2O$ source. All measurements were made relative to an isotopically enriched $^{151}Eu_2O_3$ absorber (99·15% ^{151}Eu). The isomer shift[21] of this absorber relative to $EuF_3,2H_2O$ has been determined as +0·85 mm s^{-1}, thus enabling results to be quoted relative to $EuF_3,2H_2O$. (The isomer shift for the isotopically enriched absorber differed from that for commercial Eu_2O_3). To minimise geometrical distortion, spectra were obtained by means of a stationary source and moving absorber; both source and absorber were at room temperature. The absorbers were prepared from finely ground material and each contained 10—12 mg cm^{-2} of europium.

RESULTS AND DISCUSSION

The data obtained from the Mössbauer spectra are in Table 2. A single Lorentzian peak was initially fitted to all the spectra.

It has been shown[22] that in many cases the broad lines obtained for europium compounds result from unresolved quadrupole splitting. Goodman *et al.*[23] have shown that when quadrupole splitting is taken into account, there is a discrepancy between the true isomer shift and the isomer shift obtained by analysis of spectra in terms of a single Lorentzian peak. The discrepancy is a function of the quadrupole splitting and the width of the component lines. Analysis of our data was therefore repeated by taking into account

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[23] B. A. Goodman, N. N. Greenwood, and G. E. Turner, *Chem. Phys. Letters*, 1970, **5**, 181.

quadrupole splitting, with a value of Q_{ex}/Q_{gd} of 1·3 as determined by Clifford.[24]

If it is assumed that the electric field at the ^{151}Eu nucleus has axial symmetry, the splitting of the energy levels is proportional to expression (1) where j is the

$$Q \cdot \frac{3m^2 - j(j+1)}{3j^2 - j(j+1)} \qquad (1)$$

spin of the nuclear energy state, and m is the Z component of j. For the case of europium-151, j is $\frac{7}{2}$ for the excited state, and $\frac{5}{2}$ for the ground state. From expression (1) the relative positions of transitions permitted by the selection rules can be calculated. The relative displacements of the component peaks from the centroid and their relative intensities, derived from Clebsch–Gordon coefficients, were incorporated in our curve-fitting programme. Ths actual shifts (in mm s^{-1}) were obtained by multiplication of the relative displacements by the quadrupole splitting term $\frac{1}{4}V_{zz}eQ_{gd}$.

TABLE 2

Mössbauer parameters of Eu^{III} chelates at room temperature

	Single Lorentzian peak analysis				Quadrupole splitting analysis	
			Isomer shift mm s^{-1} ($\pm$0·05)			
Chelate	Resonant effect ($\pm$1·0)	Line width mm s^{-1} ($\pm$0·15)	Relative to $^{151}Eu_2O_3$	Relative to $EuF_3,2H_2O$	Quadrupole splitting term mm s^{-1} ($\pm$0·2)	Isomer shift relative to $EuF_3,2H_2O$ mm s^{-1} ($\pm$0·05)
Eu(hedta),$4{\cdot}5H_2O$	8·1	2·44	−0·45	+0·40	+1·0	+0·38
H[Eu(edta)],$2{\cdot}5H_2O$	23·8	2·45	−0·21	+0·64	+0·9	+0·61
NH_4[Eu(edta)],$2H_2O$	27·1	2·91	−0·50	+0·35	+0·9	+0·34
K[Eu(edta)],$4H_2O$	14·0	2·65	−0·51	+0·34	+1·3	+0·30
Ba[Eu(edta)]$_2$,$7H_2O$	15·1	2·75	−0·44	+0·41	+1·1	+0·39
H[Eu(dcta)],$4H_2O$	8·6	2·88	−0·55	+0·30	+1·3	+0·26
NH_4[Eu(dcta)],$5H_2O$	10·1	2·73	−0·38	+0·47	+0·9	+0·45
K[Eu(dcta)],$4H_2O$	5·8	2·77	−0·36	+0·49	+1·0	+0·47
Ba[Eu(dcta)]$_2$,$11H_2O$	5·9	2·44	−0·37	+0·48	+1·2	+0·43
$(NH_4)_2$[Eu(dtpa)],$2H_2O$	9·1	2·34	−0·33	+0·52	+1·1	+0·49
Ba[Eu(dtpa)],$7{\cdot}5H_2O$	13·2	2·63	−0·47	+0·38	+0·8	+0·37
Eu(AcCHAc)$_3$,$3H_2O$	3·9	2·80	−0·49	+0·36	−1·7	+0·42
Eu(tta)$_3H_2O$	1·9	2·43	−0·44	+0·41	−0·7	+0·41
(pip)[Eu(BzCHAc)$_4$]	0·9	2·23	−0·61	+0·24	−1·5 +1·6	+0·34 +0·37
Na[Eu(BzCHAc)$_4$]	3·0	2·16	−0·30	+0·55	+1·3	+0·46
K[Eu(BzCHAc)$_4$]	1·2	2·44	−0·52	+0·33	+1·1	+0·31
(py)[Eu($CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3$)$_4$]			No effect observed			
Et_4N[Eu($CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3$)$_4$]	0·6	2·78	−0·42	+0·43	−3·6 +1·6	+1·00 +0·35
Me_4N[Eu($CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3$)$_4$]	0·7	3·66	+0·1	+0·95	−2·1 +2·0	+1·04 +0·72
(isoq)[Eu(tta)$_4$]	1·6	2·36	−0·41	+0·44	+1·7	+0·31
Eu(phen)(BzCH·CO·CF_3)$_3$	0·6	2·05	−0·57	+0·28	−1·7 +0·6	+0·45 +0·28
Eu(phen)(tta)$_3$			No effect observed			
Eu(phen)$_3$(CNS)$_3$	0·9	3·03	−0·26	+0·59	−1·8 +3·2	+0·60 +0·19
Eu(phen)$_2$$Cl_3$,$2H_2O$	6·5	2·32	−0·30	+0·55	−1·2 +1·2	+0·60 +0·49
Eu(phen)$_2$(benzoate)$_3$	3·9	3·51	−0·56	+0·29	−2·2	+0·41
Eu(phen)$_2$(*p*-hydroxybenzoate)$_3$	2·4	2·44	−0·27	+0·58	−1·1	+0·63
Eu(phen)$_2$(salicylate)$_3$			No effect observed			
$Eu_2(C_2O_4)_3,10H_2O$	17·8	2·10	−0·54	+0·31	+0·6	+0·31
$Eu_2(CH_2{\cdot}C_2O_4)_3,5H_2O$	16·8	2·15	−0·66	+0·19	+0·8	+0·17
$Eu_2([CH_2]_2{\cdot}C_2O_4)_3,5H_2O$	10·5	2·23	−0·48	+0·37	+0·8	+0·36
$Eu_2([CH_2]_3{\cdot}C_2O_4)_3,5H_2O$	3·2	2·14	−0·45	+0·40	+0·8	+0·37
Eu(picNO)$_3$$Cl_3$	2·6	2·0	−0·23	+0·62	−1·1 +1·2	+0·67 +0·56
Eu(tropolonate)$_3$	2·5	2·1	−0·62	+0·23	−1·3	+0·33

The variable parameters in the programme are the baseline, width of component peaks, isomer shift, effective peak height, and the quadrupole splitting term. The effective peak height, H, is the sum (2) of the heights of the eight constituent peaks, $\sum_{i=1}^{8} h_i$, and is therefore the height which would be observed if the quadrupole splitting term was zero. Since the total area, A, under the peak is given by expression (3) and

$$H = \sum_{i=1}^{8} h_i \qquad (2)$$

$$A = \frac{\pi}{2}\sum_{i=1}^{8} h_i\Gamma_i = \frac{\pi}{2}H\Gamma_{const} \qquad (3)$$

since Γ_{const}, the width of the constituent peaks, varies little from one compound to another, H can be used as a measure of the absorption intensity.

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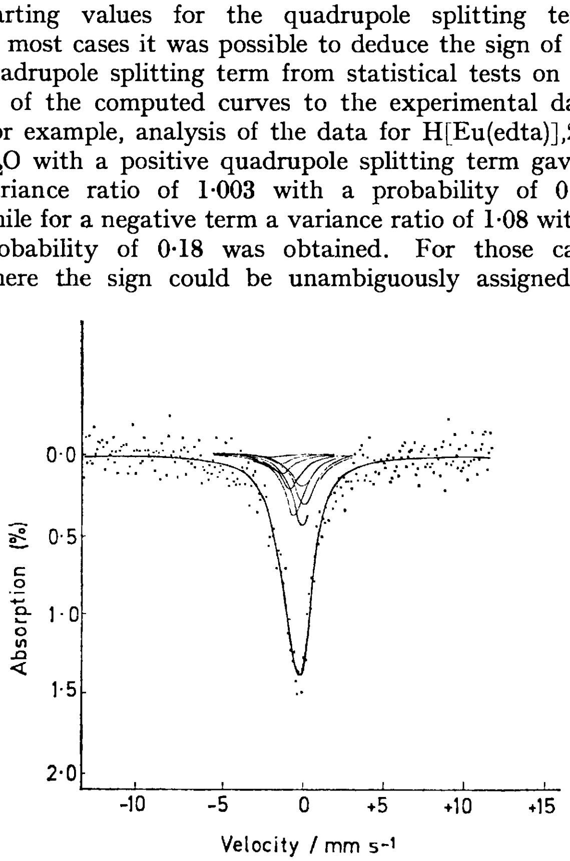
The Mössbauer parameters were computed twice for each spectrum, once with positive and once with negative starting values for the quadrupole splitting term. In most cases it was possible to deduce the sign of the quadrupole splitting term from statistical tests on the fit of the computed curves to the experimental data. For example, analysis of the data for H[Eu(edta)],2·5-H_2O with a positive quadrupole splitting term gave a variance ratio of 1·003 with a probability of 0·47, while for a negative term a variance ratio of 1·08 with a probability of 0·18 was obtained. For those cases where the sign could be unambiguously assigned in this way the preferred result is given (Table 2); for the remainder both resultant values are given. An example of curves fitted by this procedure by use of the preferred sign of the quadrupole splitting term is given in the Figure (isomer shift values relative to a $^{151}Eu_2O_3$ absorber). The Figure illustrates the way in which the eight components of the quadrupole split spectrum contribute to the observed experimental spectrum. It can be seen that in general a satisfactory fit to the experimental points has been obtained, but the Figure reveals that the fitted curve has a bias at the shoulder on the positive isomer shift side of the curve. This bias is thought to be due to the asymmetry in the fitted curve being greater than that in the experimental curve. Studies of the spectral shape as function of asymmetry parameter[25] have shown that the envelope has greater asymmetry at low values of the asymmetry parameter, and thus the observed deviations may arise from failure to take into account the possibility of a non-zero asymmetry parameter.



Mössbauer spectrum of Na[Eu(BzCHAc)$_4$]. Eight component quadrupole splitting analysis. Spectra obtained at 293 K with a $^{151}SmF_3,2H_2O$ source

Table 2 shows that small negative isomer shift values (relative to an isotopically enriched $^{151}Eu_2O_3$ absorber) were obtained for all Eu^{III} complexes which gave observable spectra at room temperature. When allowance is made for the isomer shift of the $^{151}Eu_2O_3$ absorber, relative to $EuF_3,2H_2O$ (+0·85 mm s^{-1}), it can be seen that these complexes have small positive shifts relative to $EuF_3,2H_2O$.

The following complexes failed to show any resonant absorption at room temperature; Eu(phen)$_2$(salicylate)$_3$; (py)Eu[Bz·CHAc)$_4$]; and Eu(phen)(tta)$_3$ (ligand abbreviations given in footnotes to Table 1).

Resonant Effect.—The resonant effect values, determined as the area under the curve of resonant absorption, were measured with the same $^{151}SmF_3,2H_2O$ source and with an almost constant thickness of europium in the absorbers; thus the measured values can be compared for the different compounds. Table 2 shows that the resonant effect values of the Eu^{III} β-diketone and 1,10-phenanthroline types of complex are significantly smaller than corresponding values for the aminopolycarboxylate and oxalato-types of chelate. Mackey and Greenwood[7] have suggested that the magnitude of the resonance effect can be used as an indicator of the existence of polymeric structure in Eu^{III} chelates. They correlated resonant effect values with other structural data,[26] and suggested polymeric structures for H[Eu(edta)], Eu(hedta),H_2O, and H_2-[Eu(dtpa)] on the grounds of comparatively high resonant effects. In contrast, Eu(hedta),$7H_2O$ and NH_4[Eu(edta)],$8H_2O$, which had low resonant effects, were considered to be monomeric. A comparison of our resonant effect values with those of Mackey and Greenwood shows some differences of detail; for example, we found that both H[Eu(edta)],2·5H_2O and NH_4-[Eu(edta)],$2H_2O$ gave comparatively large resonant effects. It is likely that these differences in detail are due to differences in the numbers of molecules of water associated with the chelates. However, our results show that comparatively large resonant effects are observed for aminopolycarboxylate chelates and oxalato-complexes and for these chelates carboxyl group bridging could lead to polymeric structures.

Isomer Shifts.—The range of isomer shift values reported in Table 2 is small (0·8 mm s^{-1}) and therefore for Eu^{III} complexes the measured isomer shift is insensitive to the nature of the co-ordinating ligand. It is reasonable to conclude that their bonding is predominantly ionic in character with the possibility of a small covalent contribution. In the case of the edta complexes, the isomer shift of the H^+ salt relative to $EuF_3,2H_2O$ is more positive than that of the K^+ and NH_4^+ salts. Hoard *et al.*[27-29] have shown that the H[La(edta)] salt is structurally different from the analogous K^+ and NH_4^+ salts in that the H^+ is attached

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[28] J. L. Hoard, B. Lee, and M. D. Lind, *J. Amer. Chem. Soc.*, 1965, **87**, 1611.

[29] B. Lee, M. D. Lind, and J. L. Hoard, Abstracts 152 Meeting Amer. Chem. Soc., 1966, Sect. O, Paper 70.

to a carboxyl group which is not co-ordinated to the central lanthanum ion. This structural difference could account for the more positive isomer shift value of the H^+ salt.

Mössbauer Data Analysis.—Analysis of the Mössbauer spectra described above is complicated by the effects of absorber thickness and of inherent broadening of the emission line of the source. The analysis is likely to be further complicated by a non-zero asymmetry parameter of the electric field gradient, which would change the relative intensities and positions of the lines which constitute the quadrupole-split spectrum.

By comparison of the resonance intensities and line widths obtained from a thick Eu_2O_3 absorber (30 mg cm^{-2} of Eu) and a thin Eu_2O_3 absorber, and by consideration of the data,[30] the $^{151}SmF_3,2H_2O$ source used in this work was estimated to have a recoilless fraction of *ca.* 0·25 (±0·03), and the Eu^{III} complexes were shown to have thickness parameters[30] ranging from 0·1 to 1·3. The line shapes for thickness parameters in this range do not vary significantly from a Lorentzian shape.

The magnitude of the effect of quadrupole splitting of the emission line of our $^{151}SmF_3,2H_2O$ source was studied by comparison with a 1% europium-in-palladium metal absorber which is known to have a very narrow absorption line.[31] It was found that the 1% Eu–Pd absorber, and a $^{151}EuF_3,2H_2O$ absorber, both gave very narrow line widths of respectively 1·9 ± 0·1 and 2·0 ± 0·1 mm s^{-1} when used in conjunction with the $^{151}SmF_3,2H_2O$ source. The theoretical line width[1] is 1·36 mm s^{-1}; thus the contribution of the $^{151}SmF_3,2H_2O$ source to line broadening of the absorber spectra is small and the effect on line shape can be neglected.

In the present analysis the effect of a non-zero asymmetry parameter on the positions and intensities of the lines constituting the eight-fold quadrupole split spectrum has been omitted. Inclusion of a non-zero asymmetry parameter could lead to spectral shape changes affecting isomer shift and quadrupole splitting term values. A more detailed analysis of the spectra taking into account the asymmetry parameter is therefore desirable, and will be carried out for selected spectra.

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