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A Mössbauer Effect Study of some Europium(III) Nitrate Complexes with Unidentate Oxygen-donor Ligands*

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The possibility of obtaining complexes with different coordination numbers and geometries has stimulated an interest in the preparation of europium(III) complexes with unidentate oxygen-donor ligands. Extensive work on the triphenylphosphine oxide and triphenylarsine oxide adducts with europium(III) was reported by Hart and coworkers [1, 2], who made a systematic study of their stoichiometry and coordination geometry. More recently, the single crystal X-ray structures have been determined [3] for $Eu(NO_3)_3(Ph_3PO)_3(acetone)_2$ and $Eu(NO_3)_3(Ph_3PO)_2(ethanol)$. In these compounds the europium(III) ion is coordinated to the oxygen atoms of the three triphenylphosphine oxide ligands in $Eu(NO_3)_3(Ph_3PO)_3(acetone)_2$ and to the oxygen atoms of the triphenylphosphine oxide and the ethanol ligands in $Eu(NO_3)_3(Ph_3PO)_2(ethanol)$. In both compounds the nitrate ligands are bidentate and lead to nona-coordinated europium(III) complexes. The observed geometry is very distorted and does not conform to any of the common geometries found in ennea-coordinated lanthanide compounds. Less work has been published with other oxygen-donor ligands such as hexamethylphosphoramide and pyridine *N*-oxide [4–16].

Herein we report on a series of $Eu(NO_3)_3$ complexes with these and related ligands and present a detailed analysis of their Mössbauer spectra. The Mössbauer spectra were measured in order to determine whether the europium-151 isomer shift could detect different coordination numbers and differences in the donor bonding abilities of the ligands. Furthermore, we were interested in determining whether the europium-151 quadrupole interaction could detect differences in the EFG tensor in these compounds; differences that could be related to the symmetry of the metal coordination sphere.

Experimental

All the reactants were reagent grade materials and have been used without further purification. The complexes with Ph_3PO and Ph_3AsO were prepared according to published methods [1, 2]. $Eu(NO_3)_3(DMSO)_4$ was prepared by dissolving $Eu(NO_3)_3 \cdot 5H_2O$ in dimethyl sulfoxide. Upon addition of benzene an oily material was obtained which, after standing in air for several days, was transformed into colorless needle-shaped crystals. They were washed with small amounts of ethanol and dried under vacuum over P_2O_5. The remaining complexes were prepared according to a general method in which $Eu(NO_3)_3 \cdot 5H_2O$ was dissolved in acetone or ethanol and the appropriate ligand, dissolved in the same solvent, was added in the proper stoichiometric ratio. The compounds either precipitated as white microcrystals or were obtained as oils. The oils were mixed with *n*-hexane or diethyl ether and, after 2 to 6 days in the refrigerator, white solids were obtained. In both cases the crystals were washed with small amounds of acetone, ethanol, or diethyl ether, and dried under vacuum over P_2O_5.

The compounds containing non-coordinated molecules of acetone, ethanol, or water were desolvated by heating the samples at 353 K under vacuum for 6 h. The infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer as Nujol mulls. The melting points were measured in air and are uncorrected.

The Mössbauer effect spectra were obtained on a conventional constant acceleration Mössbauer spectrometer which was calibrated at room temperature with the iron-57 Mössbauer spectrum of natural abundance α-iron foil. The europium spectra were obtained with a samarium-151 in SmF_3 source and the isomer shifts of the resulting spectra are reported relative to EuF_3. EuF_3 gave an isomer shift of 0.09 mm/s relative to α-iron foil on our spectrometer.

Results and Discussion

All the complexes are listed in Table A of the Supplementary Material together with their elemental

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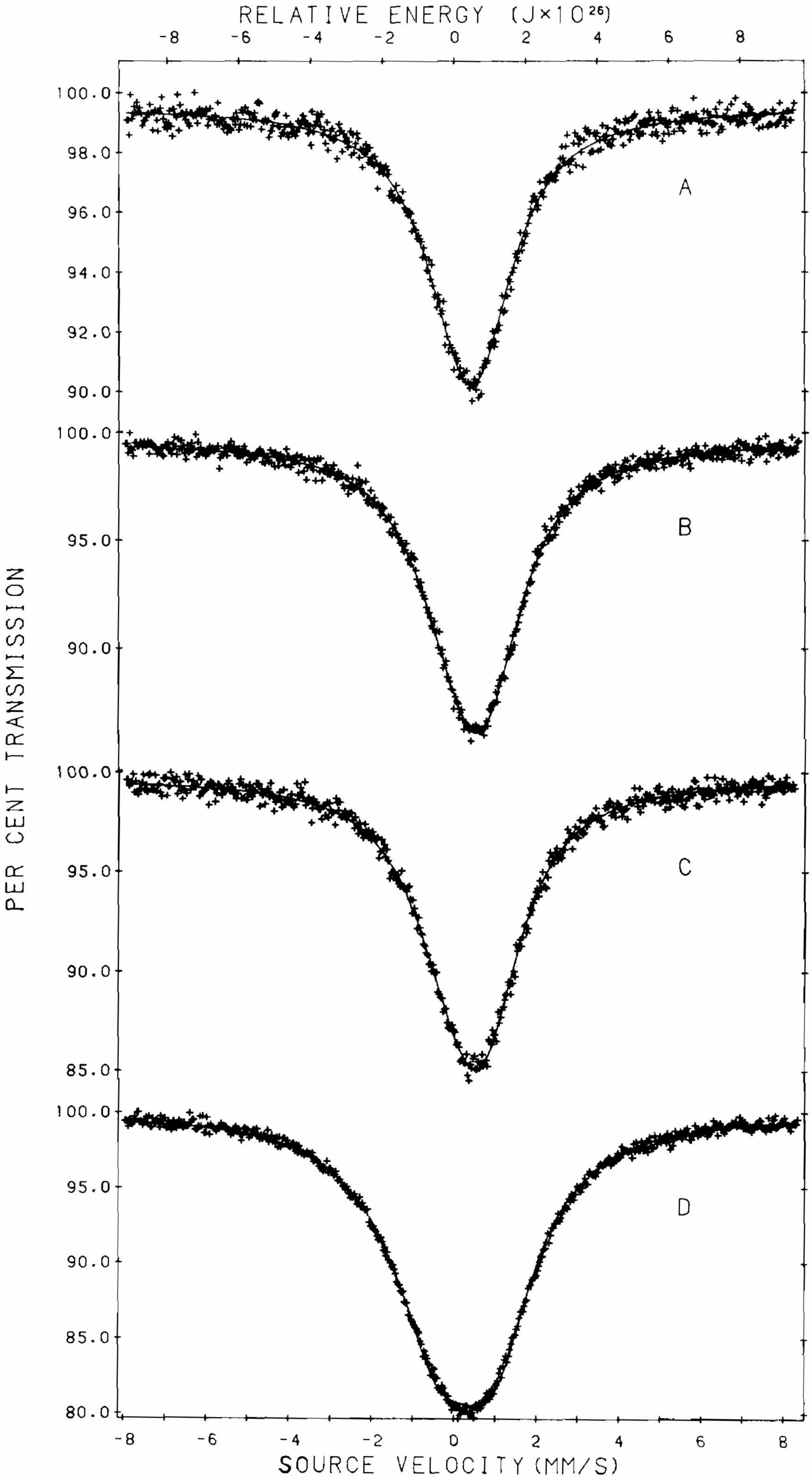

Fig. 1. The europium-151 Mössbauer spectra obtained at 78 K for: $Eu(NO_3)_3(Ph_3AsO)_3$(acetone)$_2$, (A); $Eu(NO_3)_3(Ph_3AsO)_2$(ethanol), (B); $Eu(NO_3)_3(Ph_3PO)_2$(ethanol), (C); and $Eu(NO_3)_3$(PyridineNO)$_2$(H_2O), (D).

analyses and melting points. In this Table HMPA represents the ligand hexamethylphosphoramide, DMSO the ligand dimethyl sulfoxide, and DMF the ligand dimethylformamide.

Infrared spectroscopy was useful in elucidating the structure of these compounds and the coordination sites of the various ligands. The presence of solvent molecules was detected by the strong absorption due to the carbonyl stretch in acetone, or of the hydroxyl stretch in the case of the ethanol adducts. The bidentate character of the nitrate ion was indicated by the presence of all six fundamental vibrational modes at about 1500, 1300, 1030, 800, 750 and 720 cm^{-1}. These modes seem to be a general feature in nitrate complexes with the lanthanides [17–23] and the bidentate bonding of the nitrate was verified in the previous crystal structures [3]. The stretching frequency of the N–O, P–O and S–O bonds decreases in going from the free ligands to the coordinated ligands by 15 to 40 cm^{-1}, indicating the formation of an oxygen-to-metal bond [24, 25]. A lower bond order as a consequence of the coordination is clearly the main reason for the shift of the stretching frequencies, but many other factors affect this shift. Ph_3PO [26] and HMPA show the largest shifts, whereas the Me_3NO and Ph_3AsO stretching frequencies remain virtually unaffected by the coordination. This difference may be related to the pi interaction that is very weak in Ph_3AsO and absent in Me_3NO. In contrast, the presence of the aromatic ring in the pyridine *N*-oxide permits the pi interaction and the N–O stretching frequency is shifted to lower energy [27].

The europium-151 Mössbauer effect spectra of each of the complexes revealed a broad featureless absorption band. Several typical Mössbauer spectra are illustrated in Fig. 1. Preliminary fits to a single Lorentzian line showed a range of linewidths and clearly indicated the presence of a quadrupole interaction in these compounds. Hence it was decided to fit each of the spectra to a model which included a quadrupole interaction, eQV_{zz}. In these initial fits, in which the asymmetry parameter, η, was zero, the energies of the nuclear transitions are readily calculated [28]. For europium-151 we have used 1.3 for the ratio of the nuclear quadrupole moment of the excited state to the ground state.

A Lorentzian line with a linewidth, 2Γ, was constructed for each transition with an intensity given by the Clebsch–Gordan coefficients [29]. The spectral lineshape, which is the sum of these lines, multiplied by a scaling factor, is adjusted to give the best fit to the observed spectrum. The preliminary fits using this model indicated a strong correlation between the linewidth and the quadrupole interaction. In order to overcome this problem, and to obtain eQV_{zz} values for comparison between compounds, we have constrained the linewidth, 2Γ, to 2.2 mm/s, a value which is in agreement with the observed linewidth of 2.1 mm/s in the cubic compound $Cs_2NaEuCl_6$ [30]. This value is also in agreement with the smallest linewidth of 2.3 mm/s observed in our preliminary single line fits for $Eu(NO_3)_3(Ph_3AsO)_3(acetone)_2$ and $Eu(NO_3)_3(Ph_3AsO)_4(acetone)$. The results of these fits are presented in Table I, where it is indicated that the η

TABLE I. Europium-151 Mössbauer Spectral Parameters[a]

Compound	δ (mm/s)	eQV_{zz} (mm/s)	η	Area[b] %ε (mm/s)/(mg/cm^2)
$Eu(NO_3)_3(Ph_3AsO)_3(acetone)_2$	0.30	2.60	0[c]	3.26
$Eu(NO_3)_3(Ph_3AsO)_4(acetone)$	0.48	2.71	0.2	
$Eu(NO_3)_3(Ph_3PO)_3$	0.35	2.76	0.5	2.76
$Eu(NO_3)_3(Ph_3AsO)_3$	0.29	2.83	0[c]	2.71
$Eu(NO_3)_3(Ph_3AsO)_4$	0.35	3.34	0[c]	1.72
$Eu(NO_3)_3(Ph_3PO)_3(acetone)_2$	0.31	3.51	0[c]	1.85
$Eu(NO_3)_3(Ph_3AsO)_3(ethanol)$	0.31	3.81	0[c]	1.16
$Eu(NO_3)_3(PyridineNO)_3$	0.37	4.05	0[c]	0.83
$Eu(NO_3)_3(Ph_3AsO)_2(ethanol)$	0.37	4.12	0.4	1.50
$Eu(NO_3)_3(HMPA)_4$	0.45	4.34	0[c]	1.77
$Eu(NO_3)_3(Ph_3PO)_2(ethanol)$	0.33	4.35	0[c]	1.56
$Eu(NO_3)_3(HMPA)_3$	0.33	4.58	0.8	1.86
$Eu(NO_3)_3(HMPA)_2(H_2O)$	0.35	5.20	0.5	1.80
$Eu(NO_3)_3(DMF)_3$	0.29	5.62	0[c]	0.94
$Eu(NO_3)_3(DMSO)_2(ethanol)$	0.32	6.32	0[c]	1.12
$Eu(NO_3)_3(DMSO)_4$	0.11	6.97	0.5	0.80
$Eu(NO_3)_3(Me_3NO)_3$	0.22	7.08	1.0	1.53
$Eu(NO_3)_3(PyridineNO)_2(H_2O)$	0.15	8.27	0.8	1.70

[a]All data were obtained at 78 K. The isomer shift values are given relative to EuF_3. [b]The area is given per milligram of europium(III) in the compound. [c]Value constrained to zero.

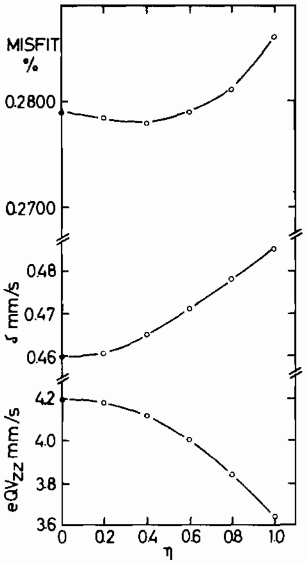

Fig. 2. The dependence of the hyperfine parameters for $Eu(NO_3)_3(Ph_3AsO)_2$(ethanol) upon η.

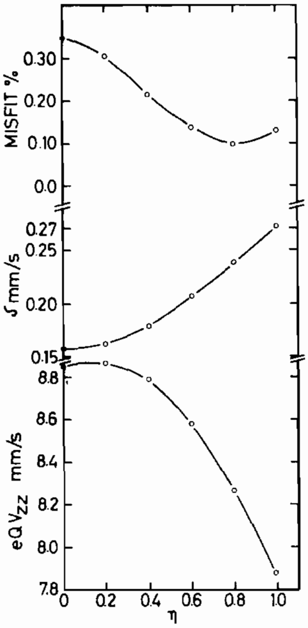

Fig. 3. The dependence of the hyperfine parameters for $Eu(NO_3)_3(PyridineNO)_2(H_2O)$ upon η.

value has been constrained to zero, and are shown as the solid lines in Fig. 1. In several instances no reasonable fits could be obtained with this model and the fits clearly indicated the presence of a non-zero asymmetry parameter.

For the fits to the spectra with a non-zero η value, the eigenvalues and eigenvectors of the quadrupole interaction Hamiltonians [31] were calculated. The energies of the transitions are determined from the eigenvalues and the intensities are determined from the eigenvectors and the Clebsch–Gordan coefficients. The Lorentzian spectral profile was calculated as for the zero η fits. The results are presented in Table I. The inclusion of a non-zero η has the effect of both broadening the spectral lineshape and making it more symmetric with increasing η. This is clearly shown in Fig. A in the Supplementary Material, which gives the calculated line shape as a function of η for a spectrum with an isomer shift, δ, of 0.05 mm/s, a quadrupole interaction, eQV_{zz}, of 7.00 mm/s, and a linewidth, 2Γ, of 2.2 mm/s. These calculations reveal a strong correlation between both the isomer shift and quadrupole interaction and the assymmetry parameter. In order to determine the influence of these correlations upon the determination of the best fit hyperfine parameters, and to estimate the errors associated with the resulting values, we have fitted several of the spectra as a function of η. The results of these fits are shown in Fig. 2 for $Eu(NO_3)_3(Ph_3AsO)_2$(ethanol) and in Fig. 3 for $Eu(NO_3)_3(PyridineNO)_2(H_2O)$ and indicate that, as the asymmetry parameter increases, the isomer shift increases and the quadrupole interaction decreases. From these results, we estimate that, for the results presented in Table I, the isomer shift values are good to ±0.02 mm/s, the quadrupole interactions to ±0.2 mm/s, and the asymmetry parameter to ±0.1.

As can be observed in Table I, these compounds have isomer shifts ranging from 0.11 to 0.48 mm/s relative to EuF_3; a range which corresponds to real differences in the s-electron density at the europium-151 nucleus. The values are very reasonable for trivalent europium nitrate complexes with oxygen donor ligands [32], but are significantly smaller than those reported by Turner [33]. At this time we have no explanation for this difference in the observed isomer shifts, but point out that those reported by Turner seem to be very high for europium(III) complexes of this type. Unfortunately, as has been noted earlier [32], there is no apparent correlation of the europium-151 isomer shift with the chemical nature of the ligands. There appears to be a slight trend to lower isomer shifts for those complexes with ligands in which the oxygen donor atom is bonded to an atom such as carbon, nitrogen or sulfur with a higher electronegativity than phosphorus or arsenic. But there appears to be little physical significance to this trend. Neither is there any correlation of the isomer shift with the molecular weight of the ligands as has been observed previously [32, 34, 35] for some europium(III) oxides and halides. From these results it would appear that the s-electron density at the nucleus in these complexes is not simply related to the electronic nature of the ligands and that covalency plays little role in the bonding of these ligands. This is not surprising and seems to point to the free ion like nature of the europium(III) ion in these complexes and the small influence that the valence bonding electrons have upon the f-electron radial distributions.

The results presented in Table I also show that there is a range of quadrupole interactions from 2.60 to 8.27 mm/s corresponding to real differences in the electronic symmetry at the europium(III) ions in the various complexes. In general the complexes containing the triphenylphosphine oxide or triphenylarsine oxide ligands have the smaller quadrupole interactions, whereas the complexes containing the DMF, HMPA, Me_3NO and DMSO ligands have the larger quadrupole interactions. This indicates that the ligands with the lower electronegativity atoms bonded to the donor oxygen atom produce, in combination with the three bidentate nitrate ligands, a more symmetric electronic environment at the europium(III) ion. Unfortunately, once again there seems to be no real molecular basis for understanding the origin of these differences. In this case more detailed single crystal X-ray structural work might lead to an understanding of the differences based upon the details of the coordination geometry.

Supplementary Material

Table A of elemental composition and melting points and Fig. A of europium-151 Mössbauer lineshapes are available from the authors.

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References

1 D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem., 29,* 1745 (1967).
2 D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem., 29,* 2965 (1967).
3 G. Valle, G. Casotto, P. L. Zanonato and B. Zarli, *Polyhedron, 5,* 2093 (1986).
4 E. Giesbrecht and L. B. Zinner, *Inorg. Nucl. Chem. Lett., 5,* 575 (1969).
5 J. T. Donohue, E. Fernandez, J. A. McMillan and D. A. Peters, *J. Inorg. Nucl. Chem., 31,* 1431 (1969).
6 J. T. Donohue and D. A. Peters, *J. Inorg. Nucl. Chem., 31,* 467 (1969).
7 L. B. Zinner and G. Vicentini, *Inorg. Chim. Acta, 15,* 235 (1975).
8 E. Giesbrecht and M. Kawashita, *J. Inorg. Nucl. Chem., 32,* 2461 (1970).
9 M. K. Kuya and O. A. Serra, *J. Coord. Chem., 10,* 13 (1980).
10 A. Seminara and E. Rizzarelli, *Inorg. Chim. Acta, 40,* 249 (1980).
11 C. H. Harrison and W. H. Watson, *J. Inorg. Nucl. Chem., 32,* 2255 (1970).
12 A. Musumeci and A. Seminara, *Inorg. Chim. Acta, 54,* L81 (1981).
13 L. B. Zinner and G. Vicentini, *J. Inorg. Nucl. Chem., 37,* 1999 (1975).
14 M. K. Kuya, O. A. Serra and V. K. L. Osorio, *J. Inorg. Nucl. Chem., 37,* 1998 (1975).
15 O. A. Serra, M. Perrier, V. K. L. Osorio and Y. Kawano, *Inorg. Chim. Acta, 17,* 135 (1976).
16 S. P. Sinha, *Z. Anorg. Allg. Chem., 434,* 277 (1977).
17 L. A. Aslanov, L. I. Soleva and M. A. Porai-Koshits, *Zh. Strukt. Khim., 13,* 1101 (1972).
18 L. A. Aslanov, L. I. Soleva and M. A. Porai-Koshits, *Zh. Strukt. Khim., 14,* 1064 (1973).
19 K. K. Bhandary and H. Manohar, *Acta Crystallogr., Sect. B, 29,* 1093 (1973).
20 K. K. Bhandary, H. Manohar and K. Venkatesan, *J. Chem. Soc., Dalton Trans.,* 288 (1975).
21 K. K. Bhandary, H. Manohar and K. Venkatesan, *Acta Crystallogr., Sect. B, 32,* 861 (1976).
22 B. Eriksson, L. O. Larsson, L. Niinistö and J. Valkonen, *Inorg. Chem., 19,* 1207 (1980).
23 M. De Matheus, J. L. Brianso, X. Solans, G. Germain and J. P. Declercq, *Z. Kristallogr., 165,* 233 (1983).
24 J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc., 83,* 3770 (1961).
25 R. L. Carlin, *J. Am. Chem. Soc., 83,* 3773 (1961).
26 F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.,* 2199 (1960).
27 S. H. Hunter, V. M. Langford, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A,* 305 (1968).
28 B. A. Goodman, N. N. Greenwood, and G. E. Turner, *Chem. Phys. Lett., 5,* 181 (1970).
29 E. U. Condon and G. H. Shortley, 'The Theory of Atomic Spectra', Cambridge University Press, Cambridge, U.K., 1935, p. 76.
30 I. Felner and I. Nowik, *Solid State Commun., 28,* 67 (1978).
31 A. L. Nichols, N. R. Large and G. Lang, *Chem. Phys. Lett., 15,* 598 (1972).
32 C. M. P. Barton and N. N. Greenwood, in J. G. Stevens and V. E. Stevens (eds.), 'Mössbauer Effect Data Index', Plenum, New York, 1973, p. 395.
33 G. E. Turner, *Ph.D. Thesis,* University of Newcastle-upon-Tyne, U.K., 1972.
34 A. J. F. Boyle and G. J. Perlow, *Bull. Am. Phys. Soc., 10,* 482 (1965).
35 G. W. Dulaney and A. F. Clifford, in I. J. Gruverman (ed.), 'Mössbauer Effect Methodology', Vol. 6, Plenum, New York, 1970, p. 65.