The Nuclear Quadrupole Interaction of ^{199m}Hg-Cysteine and ^{199m}Hg-tert-butyl-mercaptide *

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The nuclear quadrupole interaction of ^{199m}Hg in Hg-cysteine and Hg-tert-butyl mercaptide was determined at room temperature by perturbed angular correlations. The dramatic difference in the interaction strength between both compounds is a result of the two-fold and four-fold sulfur coordination, respectively. Moreover, we compared the preparation of Hg-cysteine using a Hg:cysteine ratio of 1:2 and using carrier-free ^{199m}Hg from ISOLDE/CERN and obtained identical results.

1. Introduction

Recently, we have started to investigate the nuclear quadrupole interaction (NQI) of ^{199m}Hg in a series of mercaptides [1] by time differential perturbed angular correlations (TDPAC). Although ^{199m}Hg is not a very favourable TDPAC-isotope (the intermediate state with $I=5/2$ has a halflife of 2.3 ns only, the 158 keV transition is highly converted; however, the anisotropy of the 374 keV–158 keV cascade is high), it nevertheless allows access to Hg NQI studies, especially since the only suitable isotope with $I>1/2$ in the groundstate, namely ^{201}Hg, is difficult to use in NQR spectroscopy. Moreover, it has $I=3/2$, which makes the determination of the asymmetry parameter tedious. The other alternative, conversion electron-γ TDPAC on ^{197m}Hg, which is pursued extensively by the Lisbon group at ISOLDE/CERN, is not suitable for chemical applications due to the requirement of low energy electron detection.

In this paper we report on TDPAC studies of two compounds whose single crystal X-ray structure was previously determined. This allows to establish a more quantitative correlation between observed hyperfine parameters and structural parameters. Hg-cysteine with a two-fold S-ligation [2] and Hg-tert-butyl-mercaptide with a truly polymeric structure [3] appear to be ideal candidates for this purpose.

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2. Experimental

The experiments were carried out using the high efficiency Munich TDPAC-setup [4] and a conventional 4-detector spectrometer at ISOLDE/CERN, both equipped with BaF_2-szintillators to achieve an instrumental resolving time of 450–600 ps. The ^{199m}Hg was obtained in two different ways:

(i) ^{198}HgO, enriched to 97%, was irradiated with a thermal neutron flux of $1.2 \cdot 10^{13}$ n/cm^2 s for about one hour at the Forschungsreaktor München (FRM); this yields a specific activity of about 20 mCi/g. We used typically 1 mg HgO for our sample preparation.

(ii) ^{199m}Hg from the radioactive beam at the isotope separator ISOLDE/CERN was implanted into ice at 100 K. In this way we obtained essentially carrier-free activity. The main contamination was ^{199g}Hg which we estimate to be a factor of 100–1000 more than ^{199m}Hg.

In case (i), HgO was dissolved in acetic acid after the neutron activation and added to a concentrated solution of cysteine (cys) in water with the ratio Hg:cys = 1:2.2. The $Hg(cys)_2$ precipitates first, but subsequently redissolves. Therefore we evaporated the solution to dryness. In the case of tert-butyl-mercaptan (tert) we used a large excess of tert and $Hg(tert)_2$ precipitates in the form of polymeric chains. The supernatant tert was not removed because it apparently contained no activity.

In case (ii), the ice with ^{199m}Hg implanted was thawed and added directly to the concentrated cys solution. This solution was subsequently evaporated to dryness. This procedure may be called the "infinite

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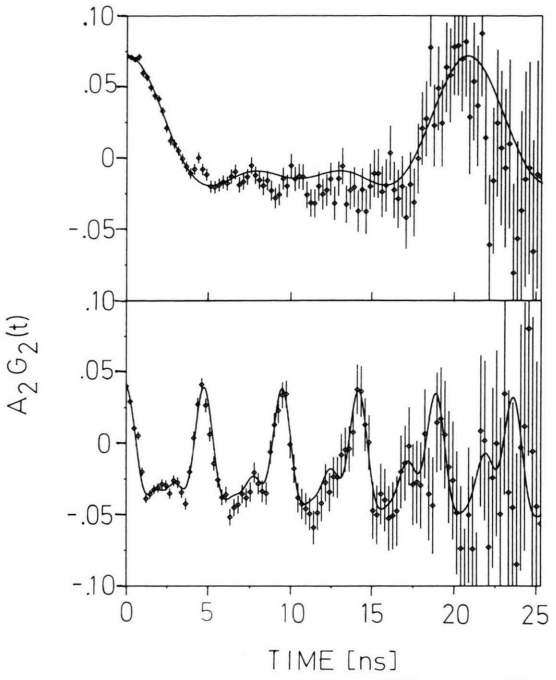

Fig. 1. TDPAC spectra for the NQI of ^{199m}Hg in ^{199m}Hg-tert-butyl-mercaptide (top) and ^{199m}Hg-cysteine (bottom) at 300 K.

Table 1. Hyperfine parameters for the NQI of ^{199m}Hg complexes.

System	Method	ν_Q [MHz]	η	Reference
cys	(i)	1409(16)	0.149(17)	this work
cys	(ii)	1407(26)	0.166(31)	this work
tert	(i)	353(4)	0	this work
DMB	(i)	1220(14)	0.213(10)	[1]
DMB	(ii)	1233(19)	0.158(24)	this work

cys=cysteine, tert=tert-butyl-mercaptide, DMB=dimercaptobenzene, (i) stoichiometric, (ii) "infinite dilution".

dilution" method. Finally, we also performed with this method a comparative study of Hg-dimercaptobenzene (DMB) which has been previously studied by method (i) [1]. It was assumed that Hg-DMB precipitates also in the "infinite dilution" case as in the stoichiometric preparation.

3. Results

Typical TDPAC spectra for $Hg(tert)_2$ and $Hg(cys)_2$ at 300 K obtained by method (i) are shown in Figure 1. It is clear that the NQI in $Hg(tert)_2$ is about a factor of four smaller than in $Hg(cys)_2$. Moreover, we find axial symmetry of the electric field gradient (EFG) in $Hg(tert)_2$, whereas in $Hg(cys)_2$ there is a small but finite deviation from axial symmetry. Essentially the same results were obtained for $Hg(cys)_2$ prepared by method (ii). In Table 1 all results obtained at 300 K for the cysteine complex, for the tert-butyl mercaptide, and for dimercaptobenzene are listed. It is clear from this table that both preparation methods yield the same results within experimental accuracy.

4. Discussion

4.1. Comparison of Preparation Methods

First, it is somewhat surprising that the "infinite dilution" method (ii) yielded exactly the same NQI parameters as the stoichiometric preparation method (i). In fact, there was no indication for any frequency distribution in both cases. The two possibilities to explain this observation are:

a) The NQI of an isolated molecule embedded in an excess of cysteine yields exactly the same NQI as in the crystalline state of the complex. This would require a very local range of contributions to the total EFG.

b) During evaporation of the cysteine solution crystallites, possibly of nanometer size, form despite the extreme dilution of $Hg(cys)_2$ molecules.

Our previous experience with $^{99}Mo(\beta^-)^{99}Tc$ NQI in Mo(V, VI)-cysteine complexes either in the crystalline state or in a frozen solution [5] suggests that the first possibility is not as unlikely as one might expect. Very similar results were obtained for $^{99}Mo(\beta^-)^{99}Tc$ in Mo(V, VI)-EDTA complexes in the crystalline state or in a frozen solution [6], which is – of course – less surprising for a chelator.

In the case of the DMB complex prepared by method (i) we believe to have formed truly polymeric chains. In this case we have to conclude that also by the method of "infinite dilution" polymeric chains are formed which then precipitate. They might be of different molecular weight compared to the concentrated case, of course. In any case, the NQI must be of a very local nature because the configuration of more distant neighbours has no effect on the EFG whatsoever.

4.2. Hg-(cysteine)$_2$

The crystal structure of $Hg(cys)_2$ was determined by Taylor et al. [2] and is shown in Figure 2. Mercury

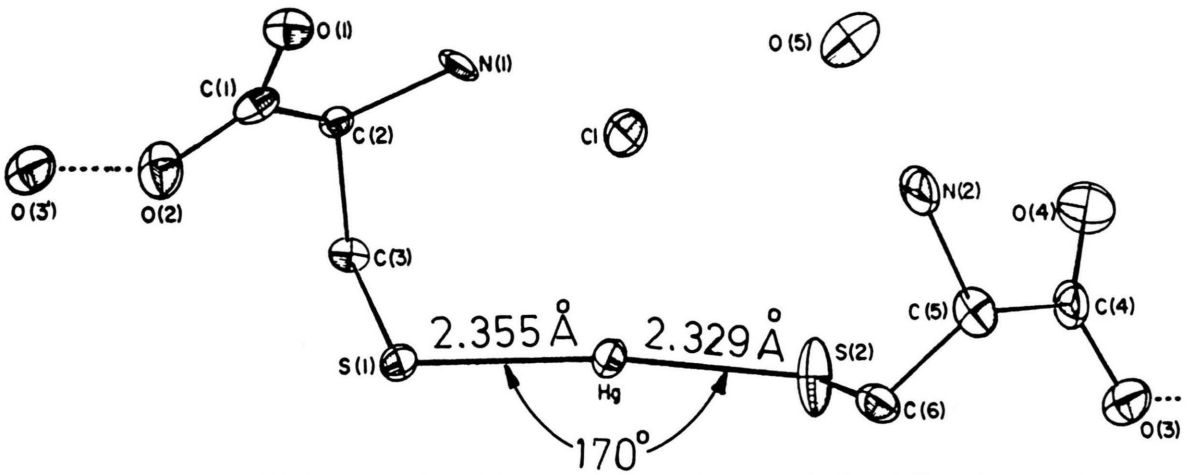

Fig. 2. Crystal structure of Hg(cysteine)$_2$ after [2] showing the almost linear coordination of Hg with two sulfur atoms.

has two sulfur ligands at distances of 2.355(3) Å and 2.329(3) Å, respectively, forming an angle of 169.8(1)°. The distance to the Cl^- ion is much larger: 3.232(5) Å. Therefore, to a good approximation we could neglect the effect of this ligand for the NQI. We believe that the deviation of the S–Hg–S bond angle from 180° reflects the influence of the distant Cl^- ion. This bond angle of about 170° is responsible for the small but finite asymmetry parameter η. In a simple nearest neighbour point charge picture [1] we would expect $\eta = 0.012$ for an angle of 170°, a little low compared to the experimental value. This picture is clearly oversimplified.

The absolute value of the NQI frequency $\nu_Q = e^2qQ/h$ is quite typical for complexes with an almost linear S–Hg–S coordination like benzylmercaptan, dithiotreitol, and glycoldimercaptoacetate [1]. As soon as the thiol group is directly attached to the benzene ring as in dimercaptobenzene the NQI is significantly lower by as much as 10–15% [1].

4.3. Hg-tert-butyl mercaptide

The crystal structure of this truly polymeric chain compound has been determined by Kunchur [3] and is shown in Figure 3. Mercury is surrounded by four sulfur atoms in a distorted tetrahedral configuration. Hg_1 and Hg_2 are crystallographically inequivalent as far as the orientation of the ligands is concerned. However, the largest component of the EFG, V_{zz}, points along the chain axis and since we have axial symmetry, both Hg-sites are identical as far as the NQI is concerned. This would even be true for single crystal studies. The bond distances are pairwise slightly different: 2.59 Å and 2.66 Å with a quoted error limit of 0.025 Å. The S–Hg–S bond angles are $87 \pm 1.5°$ and $90 \pm 1.5°$, respectively, very different from the tetrahedral angle. Since the bond angles and distances are not exactly the same we should expect a small deviation from axial symmetry. This could, however, be much too small to be detectable within the present accuracy. On the other hand, the differences obtained in the crystal structure refinement are so small compared to the experimental accuracy that we can safely neglect them. In this case we would obtain $\eta = 0$ exactly due to symmetry. This is immediately clear from the definition of the EFG-tensor: the sign of the coordinates of the charge density distribution does not enter into the EFG and we could e.g. replace the actual crystal structure by a hypothetical one with all ligand atoms being replaced by "half an atom" at the true lattice site $\boldsymbol{r}$ and another "half an atom" at the site $-\boldsymbol{r}$ obtained by inversion. This shows that we actually have a four-fold rotation axis as far as the EFG is concerned although the crystal symmetry has a two-fold rotation axis only.

In a nearest neighbour point charge estimate we obtain: $V_{zz} = 4Z(3\cos^2\phi - 1)/r^3$ with Z denoting the effective charge on S, r being the Hg–S distance, and ϕ being half the short S–Hg–S bond angle. In our case we have $\phi = 45°$ for simplicity. Hence we obtain $V_{zz} = 2Z/r^3$. Rather than to speculate about the absolute magnitude of the EFG using Sternheimer antishielding factors etc. we want to compare this result

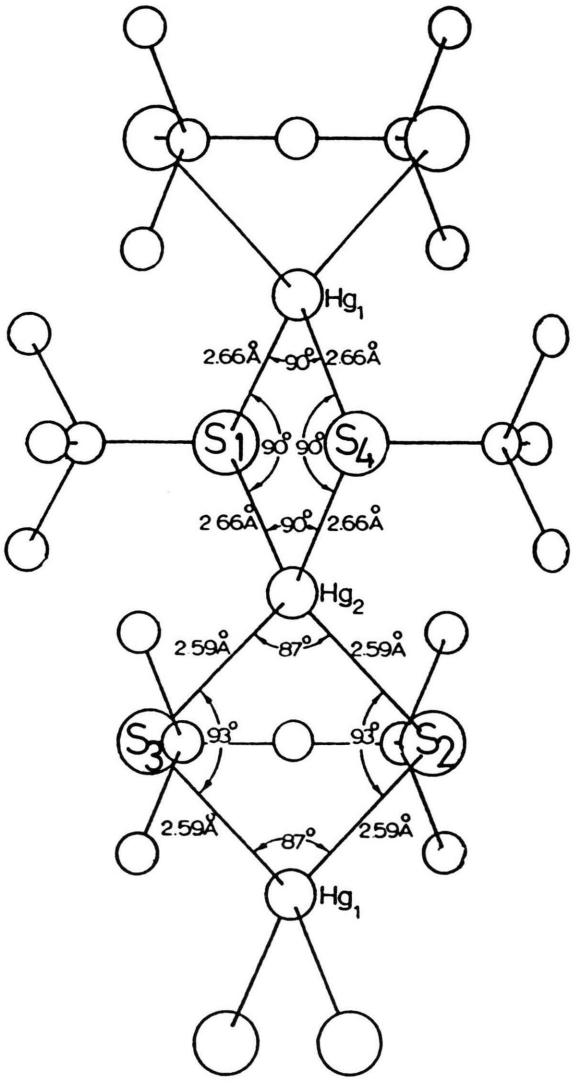

Fig. 3. Crystal structure of Hg-tert-butyl-mercaptide after [3] showing the distorted tetrahedral coordination of Hg with sulfur. The chain axis runs vertically.

with that of the linear bond system $Hg(cys)_2$. Neglecting the deviation of the S–Hg–S bond angle from 180° we obtain in the same approximation $V_{zz}=4Z/r^3$ and $\eta=0$. The ratio would then be:

$$\frac{V_{zz}(\text{tert})}{V_{zz}(\text{cys})}=\frac{Z(\text{tert})}{Z(\text{cys})}\cdot 0.355,$$

where we used average distances of $r=2.625$ Å and 2.342 Å, respectively. This should be compared to the experimental ratio of 0.25. Apparently, with the geometrical factor of 2 and the r^{-3} distance dependence one does not obtain agreement for identical effective charges on S. We would require $Z(\text{tert})/Z(\text{cys})=0.7$. A more adequate description would certainly require a band structure or a cluster calculation with the proper occupation numbers for the p-orbitals. We hope that our data will stimulate such calculations.

The angular overlap model, developed by Bauer et al. [7] for four- and five-fold coordinated Cd is apparently not directly applicable in the present case where two- and four-fold sulfur coordinated Hg is compared. This model, however, might be more useful when comparing various four-fold coordinated Hg atoms with different ligands, e.g. aminoacids.

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