^{129}Iodine Mössbauer Studies of the Purportedly Five-co-ordinated Compounds $\{M[N(CH_2CH_2NMe_2)_3]I\}I$, $M=Ni^{II}$ or Zn^{II}

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Summary The Mössbauer spectra of the two ^{129}I atoms in $M[N(CH_2CH_2NMe_2)_3]I_2$, M = Ni or Zn are indistinguishable; this result is contrary to the five-co-ordinated trigonal bipyramidal structure proposed for these complexes.

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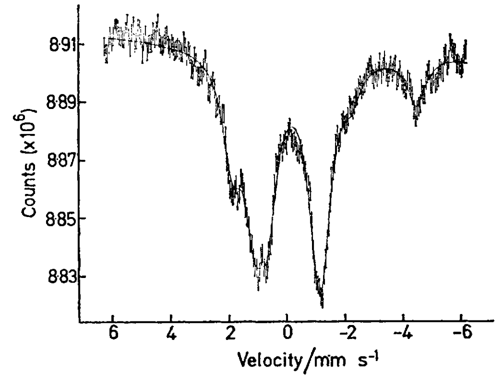
^{129}I MÖSSBAUER spectroscopy is sensitive to the distribution of iodine valence electrons and is useful for differentiating between different ligand co-ordinations. Therefore we have initiated a Mössbauer study of the bonding of iodine in various transition-metal complexes. In the course of these studies we obtained very interesting spectra for $Zn(Me_6tren)I_2$ and $Ni(Me_6tren)I_2$, $Me_6tren = N(CH_2CH_2NMe_2)_3$. This communication presents a first analysis of the data.

Ciampolini and Nardi[1] have concluded from conductivity, magnetic, and electronic absorption measurements that the quadridentate ligand Me_6tren forms five-co-ordinated complexes with first-row transition elements of the type $[M(Me_6tren)X]X$ where X = Cl, Br, I, NO_3, ClO_4, or SCN. The structures of only $[M(Me_6tren)Br]Br$ where M = Mn,[2] Fe,[2] Co,[3] Ni,[4] Cu,[4] and Zn,[2] and $[Ni(Me_6tren)NCS]SCN$[5] have been substantiated by single-crystal *X*-ray studies. Accordingly it was of interest to measure the ^{129}I Mössbauer spectra of $Zn(Me_6tren)I_2$ and $Ni(Me_6tren)I_2$.

Analytically pure samples were synthesized using ^{129}I and their physical properties agreed with those reported in the literature. The 4·2 K ^{129}I Mössbauer spectrum of a solid sample of $Zn(Me_6tren)I_2$ is shown in the Figure. Here the solid line is the result of a least-squares computer fit of a theoretical spectrum to the data (normalized $\chi^2 = 0{\cdot}8$). The spectrum shows that the two iodine atoms are equivalent with a nuclear quadrupole coupling constant of $e^2q^{129}Q = -348 \pm 25$ MHz, an isomer shift of $\delta = -0{\cdot}35 \pm 0{\cdot}05$ mm s^{-1} relative to the $Zn^{129m}Te$ source, and an asymmetry parameter of $\eta = 0{\cdot}17 \pm 0{\cdot}04$. Furthermore the spectrum of $Ni(Me_6tren)I_2$ gives the same parameters, indicating that the iodines are binding in the same way in both complexes. In addition, measurements of the complexes in a nitromethane glass (*ca.* 10^{-2}M) at 4·2 K gave the same Mössbauer parameters as in the solid state. It is clear that neither $Zn(Me_6tren)I_2$ nor $Ni(Me_6tren)I_2$ can be



FIGURE

formulated as $[M(Me_6tren)I]I$; it remains for single-crystal *X*-ray work to determine the correct structure.

One of the most important contributions of this study is a demonstration of the sensitivity of ^{129}I Mössbauer measurements for investigating the character of the bonding between an iodide ion and a transition metal. In another ^{129}I Mössbauer study of such an interaction, a quadrupole coupling constant of $e^2q^{129}Q = -1040 \pm 25$ MHz ($\delta = 0{\cdot}19 \pm 0{\cdot}05$ mm s^{-1} relative to the $Zn^{129m}Te$ source and $\eta = 0{\cdot}03 \pm 0{\cdot}03$) was found[6] for the metal-bound iodine in $[(\pi\text{-}C_5H_5)_2Ru^{129}I]^{129}I_3$. In comparison, the iodines in $Zn(Me_6tren)I_2$ and $Ni(Me_6tren)I_2$ are much more ionic than the ruthenium-bound iodine.

Preliminary ^{129}I Mössbauer measurements on $Co(Me_6tren)I_2$ show the presence of both a free iodide and a cobalt-bound iodine which is compatible with the single-crystal *X*-ray study[3] on $[Co(Me_6tren)Br]Br$. Additional ^{129}I Mössbauer experiments are planned on the other transition metal-iodine complexes in the series.

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