Mössbauer Effect Parameters in Ruthenium Compounds

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Summary The Mössbauer parameters of a series of ruthenium compounds show close analogy with those of the corresponding iron compounds and indicate the successful exploitation of the Mössbauer effect in ruthenium chemistry.

IN view of the present widespread use of the Mössbauer effect in the solution of chemical problems,[1] particularly those relating to iron and tin chemistry, it seemed important to extend the chemical applications of the Mössbauer effect to other elements. We report the isomer shifts (δ) and the quadrupole splittings (Δ) observed for some ruthenium compounds using the 90 kev transition in ^{99}Ru.

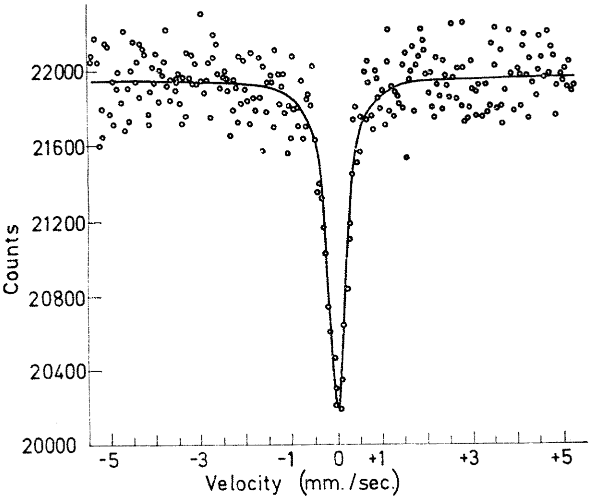

FIGURE. *Mössbauer spectrum of ruthenium metal at* 4·2° K.

The Mössbauer parameters were determined on the solid compounds using an Austin Science Associates Mössbauer Effect Spectrometer. The source consisted of approximately 7mCi of 16-day ^{99}Rh contained in a host lattice of ruthenium metal, prepared by New England Nuclear Corp., Boston, Mass. The source and absorbers were maintained at 4·2° K in a stainless steel Dewar vessel. The absorber compounds were prepared from ruthenium metal containing the natural abundance of ^{99}Ru. Absorber thicknesses were: 583 mg./cm.^{2}, ruthenium metal powder; 1670 mg./cm.^{2}, $K_2[RuCl_6]$; 810 mg./cm.^{2}, RuO_2; 688 mg./cm.^{2}, $K_3[RuCl_6]$; and 805 mg./cm.^{2}, $K_4[Ru(CN)_6]$. The isomer shifts (Table) were measured relative to a ruthenium metal absorber at 4·2° K (Figure).

Mössbauer parameters of ruthenium compounds

Compound	δ (mm./sec.)	Δ (mm./sec.)
RuO_2	$-0·22$	0·51
$K_2[RuCl_6]$	$-0·26$	0·23
$K_3[RuCl_6]$	$-0·35$	0·41
$K_4[Ru(CN)_6]$	$-0·25$	—

The isomer shift for RuO_2 is in excellent agreement with the value of $-0·24 \pm 0·05$ mm./sec. reported by Kistner.[2] The similarity in the isomer shifts for RuO_2 and $K_2[RuCl_6]$ indicates that the *s*-electron density at the nucleus of the Ru^{4+} ion in an octahedral arrangement of oxygen ligands is the same as for an octahedral arrangement of chloride ligands. The addition of one 4*d*-electron in $K_3[RuCl_6]$ causes the isomer shift to decrease. It has been shown[3] that an increase in $3d$-electron density in iron compounds results in a decrease in effective $4s$-electron density at the iron nucleus because of the increase in shielding by the d-electrons. Assuming an analogous relationship exists in ruthenium between the $4d$- and $5s$-electrons, we can conclude that the $5s$-electron density at the ruthenium nucleus is greater in $K_2[RuCl_6]$ than in $K_3[RuCl_6]$. Since an increase in s-electron density results in an increase in positive isomer shift, then the sign of the relative change in nuclear radius, $\Delta R/R$ (the nuclear parameter in the expression defining the isomer shift)[4] must be positive and opposite from that found for iron.[3]

The isomer shift for $K_4[Ru(CN)_6]$ is essentially the same as that reported for the Ru^{4+} ion. This additional increase in effective s-electron density at the nucleus in $K_4[Ru(CN)_6]$ over what would be expected for a Ru^{2+} ion is a result of the presence of back-donation of $4d$-electron density into the empty π^* CN^- orbitals. This back-donation decreases the shielding of the $5s$-electrons, thus increasing the effective s-electron density at the ruthenium nucleus. Similar results have been observed in the ferro- and ferri-hexacyanides.[5] A comparison with the analogous iron compounds, $K_4[Fe(CN)_6]$ and $SrFeO_3$,[6] indicated that the magnitude of d-electron back-donation in $K_4[Ru^{II}(CN)_6]$ is close to what it is in $K_4[Fe^{II}(CN)_6]$.

The absence of quadrupole splitting in the spectrum of $K_4[Ru(CN)_6]$ is expected for a low-spin d^6-ion where all t_{2g} orbitals are filled.[7] However, the spectrum of low-spin Ru^{3+} in $K_3[RuCl_6]$ and low-spin Ru^{4+} in $K_2[RuCl_6]$ and RuO_2 should exhibit quadrupole splitting because of partial filling of the t_{2g} orbitals. These predictions are realized, as seen in the Table. The quadrupole splitting in these compounds exists in the form of a doublet, although ^{99}Ru has a ground state spin of 5/2 and an excited state spin[2] of 3/2 and a fully resolved quadrupole split would consist of six lines. This doublet is characteristic when the quadrupole splitting of the excited 3/2 state dominates; each member of the doublet consisting of an unresolved triplet.

These results suggest that the sign of the relative change in nuclear radius ($\Delta R/R$) in ^{99}Ru is positive, and that the Mössbauer effect can be used to obtain chemically significant information about ruthenium compounds.

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