Ruthenium-99 Mössbauer Study of Ruthenium Red and its Derivatives†

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A ^{99}Ru Mössbauer study of the ions $[Ru_3(O)_2(NH_3)_{14}]^{n+}$ (n = 6 or 7) and their ethylenediamine (en) substituted derivatives, $[Ru_3(O)_2(NH_3)_{10}(en)_2]^{n+}$, has been carried out. The results support earlier proposals regarding the distribution of valence electrons on the ruthenium centres for the reduced species (n = 6). For the oxidised complexes (n = 7), however, they reveal a delocalisation of the odd electron amongst the three ruthenium centres.

The complex salt formed by the aerobic oxidation of ammoniacal solutions of ruthenium trichloride, 'ruthenium red,' has been known for some time.[1] It has been the subject of many physical and chemical studies because of its importance as a stain in electron microscopy[2] and as a probe in biological binding studies.[3] In 1960, Fletcher *et al.*[4] deduced, by chemical means, that the salt is trinuclear, $[Ru_3(O)_2(NH_3)_{14}]^{6+}$. The synthesis and *X*-ray crystal structure determination of the analogous ethylenediamine (en) substituted derivative, $[Ru_3(O)_2(NH_3)_{10}(en)_2]^{6+}$, was accomplished later,[5] and recently the structure of ruthenium red itself has been determined.[6] Both complexes were shown to be based on a linear trinuclear backbone with bridging oxo ligands, Ru–O–Ru–O–Ru.

The confirmation of the structure of these complexes has led to questions of how the valence electrons are distributed over the ruthenium centres, *i.e.* whether they are localised or delocalised. In an earlier Mössbauer study of ruthenium red and the product of its one-electron oxidation, 'ruthenium brown' $[Ru_3(O)_2(NH_3)_{14}]^{7+}$, Good and co-workers[7] attempted to solve this problem. They concluded that the valence electrons were localised in both complexes, *i.e.* that ruthenium red could be described as Ru^{3+}–O–Ru^{4+}–O–Ru^{3+} and ruthenium brown as Ru^{4+}–O–Ru^{3+}–O–Ru^{4+}. The recent *X*-ray crystallographic studies[5,6] of the complexes based on the $[Ru_3(O)_2]^{6+}$ cores apparently supported this proposal since the observed Ru–O distances in the complex differ for the terminal and central ruthenium atoms.

Since no *X*-ray structure determinations of the complexes with $[Ru_3(O)_2]^{7+}$ cores have so far been possible, the Mössbauer technique is a particularly important tool for studying the distribution of valence electrons in these cations. The present Mössbauer measurements were initiated to see if new insights could be obtained from measurements with improved statistical accuracy which have become possible since the previous study was made, and from additional measurements on the ethylenediamine derivatives of ruthenium red and ruthenium brown.

Experimental

The compounds $[Ru_3(O)_2(NH_3)_{14}]Cl_6$, $[Ru_3(O)_2(NH_3)_{14}]Cl_7$, $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_6$, and $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_7$ were prepared by published procedures.[4,5,8] The purity of the samples was confirmed by elemental analyses and ultraviolet as well as visible optical spectroscopy.

The Mössbauer studies were made at 4.2 K. The ^{99}Rh source isotope, which feeds the 89-keV Mössbauer transition after its electron capture decay to ^{99}Ru, was produced by irradiation of enriched ^{100}Ru with 35-MeV deuterons. The irradiated Ru metal was used as the Mössbauer source without further processing. The small splitting of the Mössbauer emission line arising from the electric quadrupole interaction in the hexagonal Ru matrix[9] was taken into account in the least-squares fits of the Mössbauer spectra.

Results and Discussion

The Mössbauer spectra of ruthenium red and ruthenium brown are shown in Figure 1, those of the ethylenediamine derivatives in Figure 2. All the spectra can be fitted by a superposition of two electric quadrupole patterns. We have assumed the electric field gradients to have axial symmetry and the ratio of the electric quadrupole moments of the $I = \frac{3}{2}$ excited state and the $I = \frac{5}{2}$ ground state of ^{99}Ru to be[10,11] $Q_{\frac{3}{2}}/Q_{\frac{5}{2}} = 2.94$. For the mixing ratio $E2/M1$ of electric quadrupole ($E2$) and magnetic dipole ($M1$), which determines the relative line intensities, $\delta^2 = 2.43$ was used.[11] Since the electric quadrupole splitting of the ground state is much smaller than that of the excited state, the six lines of the ^{99}Ru quadrupole patterns arise from two equally intense peaks consisting of three lines each. The sign of the electric quadrupole interaction can only be determined from the Mössbauer spectra when the quadrupole interaction is large enough for the splitting of the ground state to be at least partially resolved, as is the case when the excited state splitting $\Delta = eQ_{\frac{3}{2}}V_{zz}/2$ exceeds *ca.* 0.5 mm s^{-1}. In the present cases, positive signs for Δ generally gave slightly better fits than negative ones, but in most cases the difference is only marginal.

The uncertainty of the sign of the quadrupole interaction has little influence on the values obtained for the isomer shifts, on which the interpretation given below will mainly be based. A more serious ambiguity arises from the fact that a side-by-side and an overlapping arrangement of the two quadrupole patterns give nearly indistinguishable fits of all four spectra. As is illustrated in Figures 1 and 2, the spectral shapes corresponding to the two fitting alternatives resemble each other so closely that even a substantially improved statistical accuracy would not help to resolve the ambiguity. We therefore give the Mössbauer parameters corresponding to both solutions in the Table. Only for the overlapping solutions, and only for the pattern with the more negative isomer shift, does a positive sign for Δ give a clearly better fit than a negative one.

Disregarding the inequality of the two terminal Ru atoms in ruthenium red that arises from the twisting of one of the terminal $Ru(NH_3)_5$ groups,[6] one expects the Mössbauer spectra of all the studied complexes to consist of two quadrupole patterns with an intensity ratio of 2:1, the stronger one belonging to the two terminal ruthenium atoms, and the weaker to the central metal atom. Since the co-ordination sphere of the terminal ruthenium atoms differs from that of the central one, two different Mössbauer patterns will be observed whatever the

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

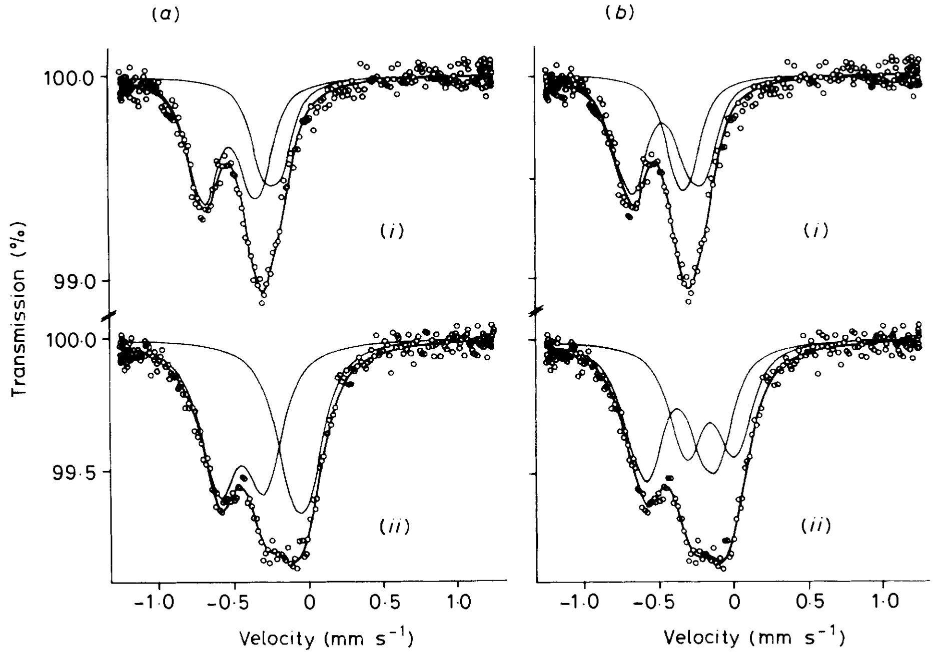

Figure 1. Mössbauer spectra of (*i*) ruthenium red, $[Ru_3(O)_2(NH_3)_{14}]Cl_6$, and (*ii*) ruthenium brown, $[Ru_3(O)_2(NH_3)_{14}]Cl_7$, fitted with a side-by-side (*a*) and an overlapping (*b*) arrangement of two quadrupole patterns

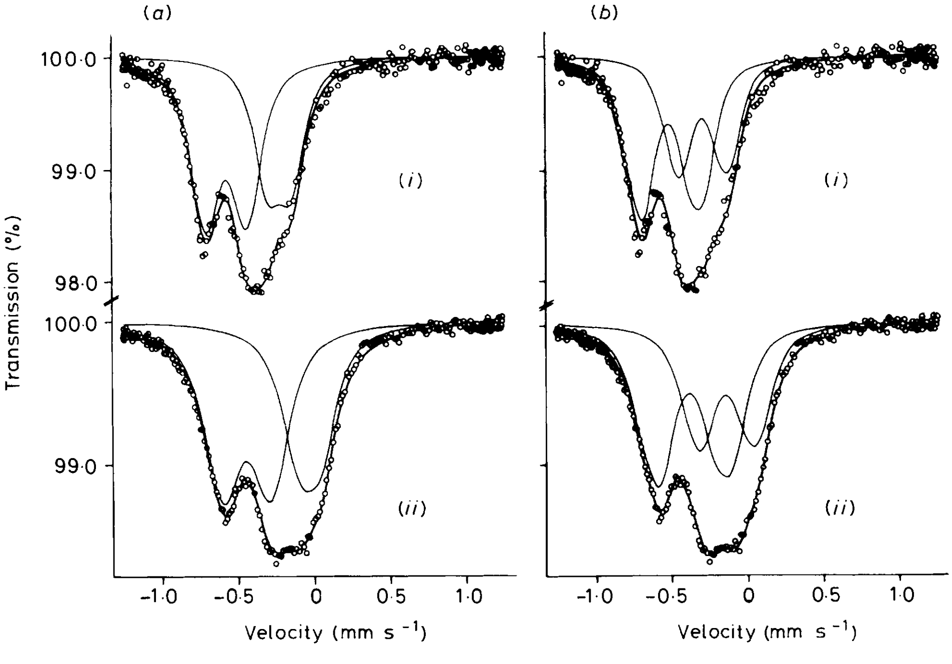

Figure 2. Mössbauer spectra of (*i*) $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_6$ and (*ii*) $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_7$ fitted with a side-by-side (*a*) and an overlapping arrangement (*b*) of two quadrupole patterns

charge distribution over the complex may be. As can be seen from the Table, the pattern with the more negative isomer shift is, in all cases, stronger than the pattern with the more positive isomer shift, although the 2:1 intensity ratio is found only for ruthenium red. In the other complexes, the contribution of the terminal ruthenium atoms is weaker than expected, presumably because the Lamb Mössbauer *f*-factors[12] of the terminal ruthenium atoms are smaller than that of the central one. This will be the case when the motional amplitudes of the terminal metal atoms are larger than those of the central one. In all cases, however, the more intense pattern has the smaller isomer shift. Since it is improbable that differences in the *f*-factors are large enough to cause an inversion of the intensity ratios in some of the complexes, but not in the others, we conclude that the terminal ruthenium atoms always give rise to a smaller isomer shift than the central one.

From the systematics of isomer shifts in ruthenium compounds[13] it is known that trivalent ruthenium has smaller isomer shifts than tetravalent ruthenium. The present Mössbauer results are thus in general agreement with the notion that

Table. Mössbauer parameters of ruthenium red and ruthenium brown and their ethylenediamine derivatives*

Compound	W	S_{3+x}	Δ_{3+x}	S_{4+y}	Δ_{4+y}	$\frac{A_{3+x}}{A_{4+y}}$
			mm s^{-1}			
$[Ru_3(O)_2(NH_3)_{14}]Cl_6$	0.188(8)	−0.517(6)	0.370(11)	−0.233(7)	0.123(14)	1.86(11)
	0.187(10)	−0.466(4)	0.476(8)	−0.331(6)	0.095(13)	2.00(9)
$[Ru_3(O)_2(NH_3)_{14}]Cl_7$	0.248(10)	−0.442(6)	0.317(8)	−0.051(5)	0.125(11)	1.37(8)
	0.217(10)	−0.372(4)	0.476(6)	−0.155(5)	0.341(8)	1.32(7)
$[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_6$	0.183(5)	−0.575(3)	0.285(4)	−0.225(3)	0.162(5)	1.46(5)
	0.155(6)	−0.524(2)	0.398(3)	−0.302(3)	0.335(5)	1.44(5)
$[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_7$	0.242(4)	−0.442(3)	0.331(3)	−0.031(3)	0.146(4)	1.55(4)
	0.200(4)	−0.380(2)	0.480(2)	−0.144(2)	0.382(3)	1.39(3)

* W = full width at half maximum of all lines, Δ = electric quadrupole splitting of the $I = \frac{3}{2}$ excited state, and S = isomer shift with respect to Ru metal. A_{3+x}/A_{4+y} is the intensity ratio of the two quadrupole patterns attributed to the terminal $[Ru^{(3+x)+}]$ and central $[Ru^{(4+y)+}]$ metal atoms. Statistical errors are given in parentheses. The first set of parameters given for each compound describes the side-by-side arrangement of the two quadrupole patterns, the second set the overlapping one.

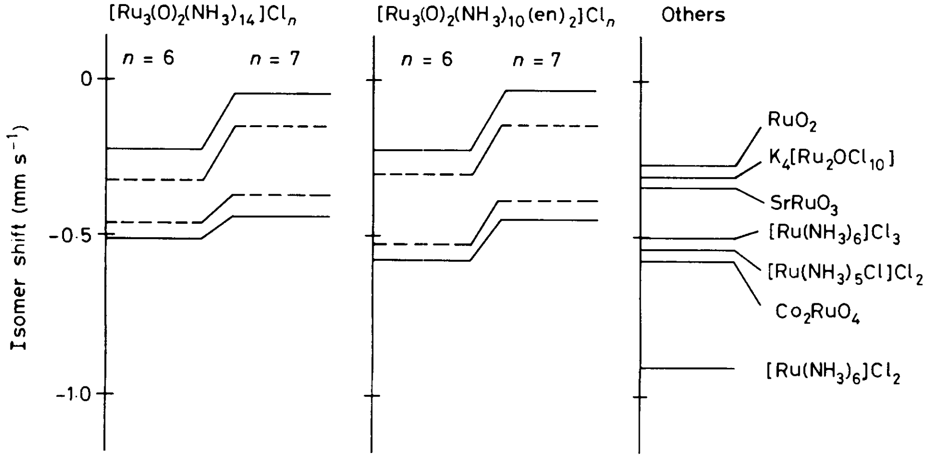

Figure 3. Comparison of the isomer shifts observed in ruthenium red, ruthenium brown, and their ethylenediamine derivatives with those found for di-, tri-, and tetra-valent ruthenium in some other compounds (ref. 13). For $[Ru_3(O)_2(NH_3)_{14}]Cl_n$ and $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_n$, the fully drawn bars represent the fits with side-by-side quadrupole patterns, the dashed bars those with overlapping ones

ruthenium red and its ethylenediamine derivative are based on a Ru^{3+}–O–Ru^{4+}–O–Ru^{3+} backbone. The formulation of ruthenium brown and its derivative as Ru^{4+}–O–Ru^{3+}–O–Ru^{4+}, however, is incompatible with the Mössbauer data. For such a complex, one would expect the Ru^{3+} and Ru^{4+} species to have practically the same isomer shifts as in ruthenium red, but the quadrupole pattern of Ru^{4+} to be about twice as strong as that of Ru^{3+}. This is not observed. Instead, in ruthenium brown as well as its ethylenediamine derivative both quadrupole patterns have somewhat larger isomer shifts than the corresponding patterns in ruthenium red and its derivative, while the pattern with the smaller shift always remains more intense. From this we conclude that the oxidation of the hexavalent cations increases the effective valencies of all three ruthenium atoms, *i.e.* that the heptavalent cations should be described as $Ru^{(3+x)+}$–O–$Ru^{(4+y)+}$–O–$Ru^{(3+x)+}$, where $2x + y = 1$. We arrive at this conclusion without giving preference to either the overlapping or the side-by-side arrangement of the two quadrupole patterns in the individual complexes. The different interpretation of the Mössbauer spectra of ruthenium red and ruthenium brown given by Good and co-workers[7] cannot merely be attributed to deficiencies in the statistical accuracy of the Mössbauer spectra reported by these authors, but arises from substantial differences between the present spectra and those of Good and co-workers, which presumably are due to impurities in the compounds used by these authors.

In Figure 3 the isomer shifts found for ruthenium red and the related compounds are compared with the shifts of other compounds of di-, tri-, and tetra-valent ruthenium[13] that appear to be relevant in the present context. The isomer shifts found in oxides as well as in complexes with NH_3 ligands suggest that the shift of Ru^{3+} and Ru^{4+} in ruthenium red and its ethylenediamine derivative should be near −0.5 and −0.25 mm s^{-1}, respectively. This expectation is met by the results of the fits with side-by-side quadrupole patterns. This interpretation is thus compatible with well localised valencies in the complexes based on $[Ru_3(O)_2]^{6+}$. The fits of the spectra with two overlapping quadrupole patterns, on the other hand, give isomer shifts that are too positive for the trivalent constituents and too negative for the tetravalent one, their difference being only about half the value expected for well localised Ru^{3+} and Ru^{4+} oxidation states. On the basis of the Mössbauer data it is impossible to distinguish between these alternatives, but at least the Mössbauer data do not disagree with the common notion that ruthenium red contains well localised Ru^{3+} and Ru^{4+} entities. It cannot be ruled out, however, that even in ruthenium red and its ethylenediamine derivative there is already a certain degree of charge delocalisation.

For the Mössbauer spectra of ruthenium brown and its ethylenediamine derivative, the ambiguity of an interpretation with side-by-side or with overlapping quadrupole pattern also exists. When the side-by-side interpretation is accepted for both the reduced and the oxidised complexes, one finds that oxidation increases the isomer shift for the terminal ruthenium atoms by 0.08 mm s^{-1} in the case of ruthenium red and brown, and by 0.13 mm s^{-1} in the case of the ethylenediamine derivatives, while the corresponding increases for the central ruthenium are about twice as large, namely 0.18 and 0.20 mm s^{-1}. Assuming a proportionality between the effective oxidation state and the isomer shift, this suggests that the oxidised complexes should be considered approximately as $Ru^{3.25+}$–$Ru^{4.50+}$–$Ru^{3.25+}$.

Conclusions

Independent of the ambiguity in the interpretation of the Mössbauer data, one can rule out the formulation of ruthenium brown, $[Ru_3(O)_2(NH_3)_{14}]Cl_7$, and its ethylenediamine derivative, $[Ru_3(O)_2(NH_3)_{10}(en)_2]Cl_7$, with Ru^{4+}–Ru^{3+}–Ru^{4+} cores. The Mössbauer isomer shifts found in these complexes rather show that the oxidation state of the terminal ruthenium atoms remain lower than that of the central one. The valence electron removed from the trinuclear complex on oxidation from the 6+ to the 7+ state can thus be considered as being smeared out over the whole complex, and its removal to lead to a valence electron distribution corresponding roughly to $Ru^{3.25+}$–$Ru^{4.50+}$–$Ru^{3.25+}$. The idea of delocalised charges in mixed-valence ruthenium complexes is not without precedent. A similar delocalization has been proposed after a comprehensive reinvestigation[14] of the Creutz–Taube anion, $[(H_3N)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ (pyz = pyrazine) by various physical techniques including Mössbauer spectroscopy.

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