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A COLOR REACTION OF AQUAHYDROGENETHYLENEDIAMINETETRAACETATO-RUTHENIUM(III) WITH SOME SULFUR COMPOUNDS

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A new color reaction of [Ru(Hedta)(H_2O)] with some compounds that contain groups C-SH or C=S has been found. Alkanethiols, cysteine, thiourea and thiosulfate assume pink to reddish brown color, while benzenethiols show blue color. It was suggested that the coloration is due to the anation of [Ru(Hedta)(H_2O)] with sulfur-containing compounds.

In the course of our study on the redox reaction of aquaethylenediaminetetraacetatoruthenate(III)[1], it was observed that the complex solution assumes an intense red color (log ε = 3.1 - 3.6) by the addition of some sulfur compounds such as cysteine, thiourea and thiosulfate (Fig. 1). As is seen from Fig. 2, the mole ratio of the complex to sulfur compounds was found to be 1:1. A mixed solution of the complex and cysteine showed new CD spectral peaks at 516 nm (+0.64), 436 nm (-0.41), 380 nm (+0.25) and 335 nm (-0.33). (The figures in parentheses are Δε values.) The reaction products were paramagnetic in both solution and solid states. The magnetic moment of the ruthenium in 0.1 M solution was evaluated as 1.91 B.M. at 24.2°C. Therefore, it may be said that +3 state of ruthenium is not changed throughout the

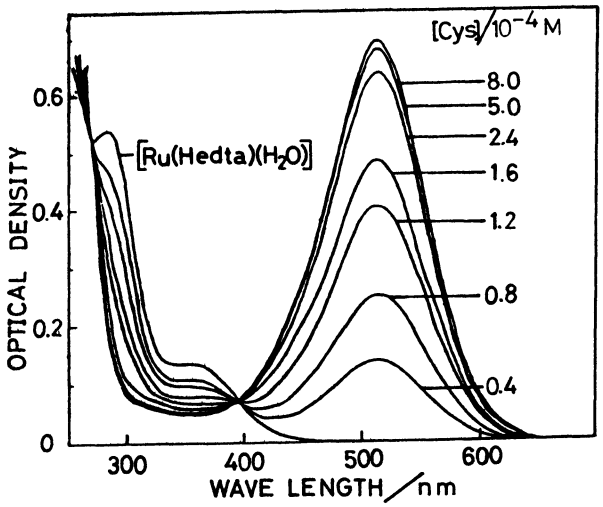

Fig. 1. Electronic spectra of [Ru(Hedta)(H_2O)] - L-cysteine system. [Ru(Hedta)(H_2O)]: 2.0 x 10^{-4}M.

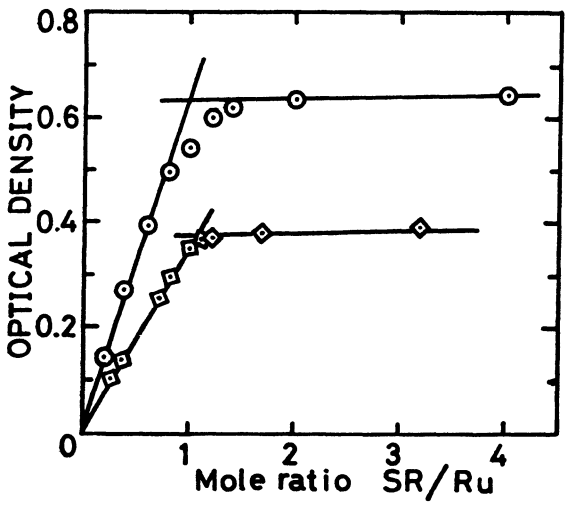

Fig. 2. Mole ratio plot. [Ru(Hedta)(H_2O)]: 2.0 x 10^{-4}M. —o—: $S_2O_3^{2-}$; —◇—: thiourea.

reaction. The existence of COO-Ru bonding was confirmed by an infrared absorption band at 1620 cm^{-1}. Furthermore, the elementary analyses of the solid products supported the ratio edta to sulfur compound to be 1:1. On the basis of these observations, it is presumed that the color reaction is an anation of the following type,

$$[Ru(edta)(H_2O)]^- + SR^{n-} \rightleftharpoons [Ru(edta)(SR)]^{(n+1)-} + H_2O \qquad (1)$$

where SR^{n-} denotes sulfur-containing anion. The nature of the color may be a charge transfer between bivalent sulfur and ruthenium(III) in the complex.

Of various sulfur compounds, alkanethiols, cysteine, O-ethyl dithiocarbonate, 2-mercaptobenzoxazole, thiourea and thiosulfate gave pink to reddish brown color, while benzenethiols showed blue color. It was noted that benzylthioacetic acid, cystine, sulfite and sulfate did not show any color. In Table 1, coloration characteristics of some typical compounds were tabulated.

Table 1. Color Reaction of $[Ru(Hedta)(H_2O)]$ at 25°C

Sulfur Compounds	λ_{max}/nm	log ε	Remarks
$1\text{-}C_4H_9SH$	527	3.61	0.1 M HOAc
$HSCH_2CH(NH_2)COOH$	512	3.54	pH 3.2
C_2H_5OCSSK	537	3.11	pH 4.7
$Na_2S_2O_3$	495	3.50	pH 4.7, after 24h
$(H_2N)_2CS$	468	3.30	pH 4.7
C_6H_5SH	608	3.62	pH 4.7, ethanol added
$o\text{-}C_6H_4(SH)COOH$	597	3.59	pH 4.7, ethanol added
"	604	3.59	0.1 M HOAc, ethanol added

The colors developed by alkanethiols and their related compounds fade slowly probably owing to the air oxidation. However, colors by benzenethiols, thiourea and thiosulfate are stable for a few days. From the spectral data of the mole ratio experiments, the equilibrium constants (log K_{AN}) of the anation reaction (1) for thiosulfate and thiourea at 25°C and I = 0.1 were calculated as 5.23 and 5.43, respectively.

It may be noted that there is a parallel between the above-mentioned color reaction and the iodine-sodium azide reaction of thiols and thiocarbonyl compounds[2]. The application of this color reaction to the identification and photometric determination of the sulfur-containing compounds has been persued.

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REFERENCES AND NOTES

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$[Ru(Hedta)(H_2O)]$ was prepared by a modified Mukaida's method (Nippon Kagaku Zasshi, 86, 598 (1965)).
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