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Catalytic Effect of Dimethylsulfoxide Complexes of Rh(III) and Ru(II) on the Polymerization of Vinyl Monomers Initiated by 2,2′-Azobisisobutyronitrile

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ABSTRACT

Transition metal salts and complexes catalyze the polymerization of vinyl monomers in the presence or absence of 2,2′-azobisisobutyronitrile (AIBN). In this article the effect of some dimethyl sulfoxide complexes of Rh(III) and Ru(II) on the polymerization of vinyl monomers such as methyl methacrylate (MMA) and methyl acrylate (MA) initiated by AIBN is reported. The percentage conversion and the rate of polymerization of MMA and MA are found to increase rapidly with time. At the critical concentrations of the complexes, the percentage conversion and the rates of reaction are found to be higher than those with AIBN alone, which significantly proves their accelerating effect. At concentrations above and below that of the critical value, the percentage conversion and the rates of polymerization of MMA and MA are found to decrease from those with AIBN alone. The trend of the increase and decrease of the percentage conversion and the rate of reaction with both types of complexes are similar. The solvent used in the polymerization of MMA and MA is dimethylsulfoxide (DMSO) and the temperature of the reaction is 60°C. A precise mechanism for the catalytic reaction is suggested.

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INTRODUCTION

Extensive work has been done on the polymerization of vinyl monomers initiated by 2-2'-azobisisobutyronitrile (AIBN) in the presence of liquid sulfur dioxide [1, 2], metal salts [3, 4], quaternary ammonium salts [5], and metal complexes [6, 7]. Ziegler-Natta catalysts occupy a special position in the polymerization of vinyl monomers in respect to initiation as well as catalytic reactions [8, 9]. Transition metals form excellent carbonyl complexes which are widely used in the polymerization of methyl methacrylate (MMA) and methyl acrylate (MA) as catalysts in absence of AIBN [10, 11]. Very little work has been done on the polymerization of MMA and MA initiated by AIBN in the presence of dimethylsulfoxide complexes of Rh(III) and Ru(II). The present work constitutes research on the catalytic effect of some dimethylsulfoxide complexes of Rh(III) and Ru(II) on the polymerization of MMA and MA in the presence of AIBN in DMSO at 60°C. The metal complexes are found to behave as accelerators as well as retarders in the polymerization of MMA and MA. The kinetic study and the mechanism of the reaction are thoroughly discussed.

EXPERIMENTAL

Materials

MMA and MA were purified [12]. AIBN was dissolved in acetone and recrystallized before use [13]. DMSO was purified [14] for experimental purposes.

Procedure

Metal complexes in DMSO were placed in a single-limbed tube fitted with a dilatometer and degassed by vacuum. The tube was sealed and after the reaction mixture was thoroughly mixed it was transferred to the dilatometer and again sealed [15]. The dilatometer was immediately immersed in a thermostat set at 60 ± 0.1°C. The percentage of polymerization and the rate of polymerization were evaluated by their volume concentration with time. The rate of polymerization and the corresponding percentage conversion for both MMA and MA with AIBN at 60 ± 0.1°C in the absence of metal catalysts were also ascertained dilatometrically for comparison with the effect of the catalyst. Characterizations of the AIBN-substituted complexes A, B, C, D, and E were done by IR analysis of the solution spectra of the mixture of each original metal complex and AIBN in DMSO. The shifting of the absorption band from 2250 cm^{-1}, which is the absorption ban od the cyano group of AIBN, to 2225-2230 cm^{-1} indicates the formation of AIBN-substituted metal complexes [16].

The complexes used in the polymerization of MMA and MA are hexakid(dimethylsulfoxide)rhodium(III)tetrafluoroborate [Rh(DMSO)$_6$(BF$_4$)$_3$ (A), trichlorotris(dimethylsulfoxide) rhodium(III) [Rh(DMSO)$_3$Cl$_3$] (B), trobromotris(dimethylsulfoxide) rhodium(III), [Rh(DMSO)$_3$Br$_3$] (C), dichlorotetrakis(dimethyl-sulfoxide)ruthenium(II), [Ru(DMSO)$_4$Cl$_2$] (D), and dibromotetrakis(dimethylsulfoxide)ruthenium-(II), [Ru(DMSO)$_4$Br$_2$] (E), These complexes were prepared as per literature [17-20].

Analysis

Calculated for A: Rh = 12.42%, S = 23.16%. Found: Rh = 12.39%, S = 23.12%.

Calculated for B: Rh = 23.22%, Cl = 24.01%. Found: Rh = 23.20%, Cl = 24.0%.

Calculated for C: Rh = 17.85%, S = 16.64%. Found: Rh = 17.81%, S = 16.60%.

Calculated for D: S = 26.41%, Cl = 14.65%. Found: S = 26.38%, Cl = 14.59%.

Calculated for E: C = 16.73%, H = 4.18%, S = 22.31%. Found: C = 16.65%, H = 4.16%, S = 22.25%.

The infrared spectra were recorded by a Specord 75 IR spectrometer. The results agree with literature data [17-20].

RESULTS AND DISCUSSION

As the polymerization of MMA and MA were carried out under vacuum dilatometrically by AIBN and metal catalysts, the reaction is initiated by a free-radical mechanism produced from AIBN at 60°C.

The relationships of the percentage conversion and R_p of MMA initiated by fixed AIBN at 60°C at the critical concentrations of Rh(III) and Ru(II) complexes are shown in Figs. 1 and 2, respectively. The plots for each metal complex under these conditions indicate that these are the accelerators in the polymerization of MMA.

The relationship of the percentage conversion and the R_p of MMA at a constant concentration of AIBN using both higher and lower concentrations of Rh(III) and Ru(II) complexes than those of the critical ranges are shown in Figs. 3 and 4, respectively. From these plots it is clear that the percentage conversion as well as R_p of MMA is lower than those with AIBN alone, indicating the retarding effect of the complexes used. Similar effects are also observed in the case of the polymerization of MA initiated by fixed AIBN in DMSO at 60°C in the presence of the same metal complexes. Only the behaviors at the critical concentrations of the Rh(III) and Ru(II) complexes are shown in Figs. 5 and 6, respectively.

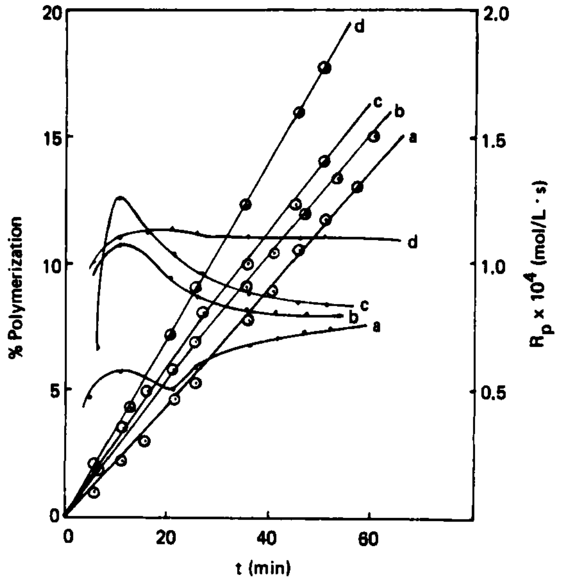

FIG. 1. Double plots of % polymerization and the rate of polymerization of MMA initiated by AIBN at 60°C and accelerated by Rh(III) complexes at their critical concentration in DMSO. [MMA] = 1.872 mol/L, [AIBN] = 0.99×10^{-3} mol/L. (a) No added rhodium complex, (b) [A] = 0.01×10^{-3} mol/L, (c) [B] = 0.03×10^{-3} mol/L, (d) [C] = 0.31×10^{-3} mol/L.

MMA and MA may be polymerized by the free radical initiation of AIBN at 60°C in DMSO. The polymerization of MMA and MA initiated by AIBN at 60°C in the presence of the complexes of rhodium(III) and ruthenium(II) used may be explained by the following mechanism [21].

Each metal complex and AIBN when dissolved in DMSO maintains an equilibrium with the AIBN-substituted complex:

$$[\mathrm{Rh}]^{3+} + \mathrm{AIBN} \rightleftharpoons [\mathrm{RhAIBN}]^{3+} \tag{1}$$

$$[\mathrm{Ru}]^{2+} + \mathrm{AIBN} \rightleftharpoons [\mathrm{RuAIBN}]^{2+} \tag{2}$$

Thermal decomposition of the initiator:

$$\mathrm{AIBN} \longrightarrow \mathrm{R}^{\cdot} \tag{3}$$

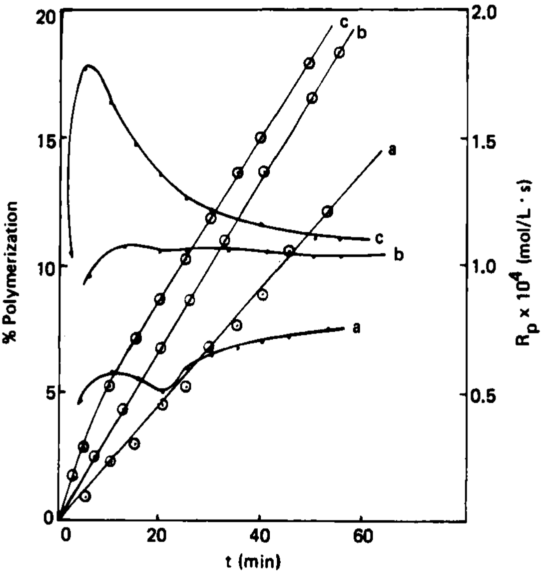

FIG. 2. Double plots of % polymerization and the rate of polymerization of MMA initiated by AIBN at 60°C and accelerated by Ru(II) complexes at their critical concentrations in DMSO. [MMA] = 1.872 mol/L, [AIBN] = 0.99 × 10^{-3} mol/L. (a) No added ruthenium complex, (b) [D] = 0.06 × 10^{-3} mol/L, (c) [E] = 0.16 × 10^{-3} mol/L.

Decomposition of the AIBN-substituted metal complex:

$$[\mathrm{RhAIBN}]^{3+} \longrightarrow \mathrm{R}^{*} \quad (4)$$

$$[\mathrm{RuAIBN}]^{2+} \longrightarrow \mathrm{R}^{*} \quad (5)$$

Initiation:

$$\mathrm{M} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{R}_1^{\cdot} \quad (6)$$

$$\mathrm{M} + \mathrm{R}^{*} \longrightarrow \mathrm{R}_1^{*} \quad (7)$$

Here $\mathrm{R}_1^{\cdot}$ and R_1^{*} are the primary free radicals. The primary free radicals attack the monomer in the subsequent propagation step. Termination may be due to decomposition, neutral combination by growing radical, and by the decay of the metal ions by the transfer of electrons from the free radicals to the metal ions.

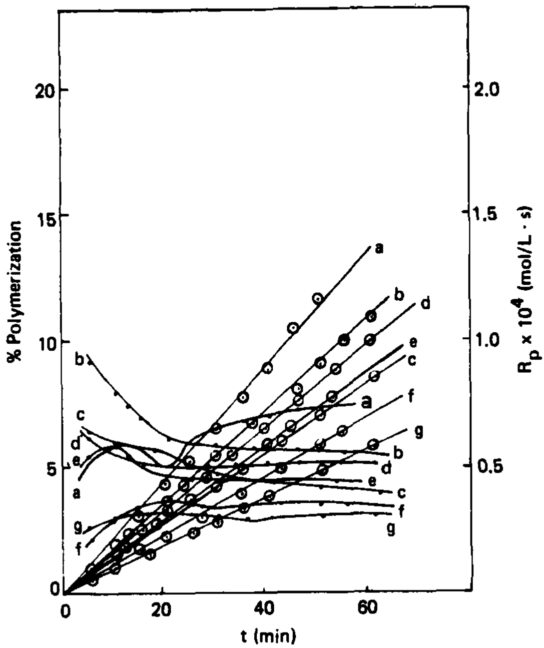

FIG. 3. Double plots of % polymerization and the rate of polymerization of MMA initiated by AIBN at 60°C and retarded by Rh(III) complexes at higher and lower concentrations than the critical range in DMSO. [MMA] = 1.872 mol/L, [AIBN = 0.99 × 10^{-3} mol/L. (a) No added rhodium complex, (b) [C] = 0.43 × 10^{-3} mol/L, (c) [C] = 0.03 × 10^{-3} mol/L, (d) [B] = 0.06 × 10^{-4} mol/L, (e) [B] = 0.06 × 10^{-3} mol/L, (f) [A] = 0.02 × 10^{-3} mol/L, (g) [A] = 0.06 × 10^{-4} mol/L.

Characterization of the AIBN-substituted complexes of A, B, C, D, and E has been done by IR analysis by taking the solution spectra of the complexes with AIBN in DMSO separately under vacuum. The shifting of the absorption band from 2250 cm^{-1}, which is due to the vibration of CN groups in AIBN, to 2225-2230 cm^{-1} indicates the coordination of the nitrile group of AIBN to the metal ions. These AIBN-substituted complexes of A, B, C, D, and E undergo decomposition to the more active free radicals R* along with the simultaneous decomposition of free AIBN thermally to the free radical R· at 60°C as shown in Reactions (3), (4), and (5).

When the amount of metal complexes added is low, the concentration of the AIBN-substituted complex will also be low, and a part of the substituted complex decomposes to produce R* at 60°C. Therefore the rate of polymerization of the monomers will be less

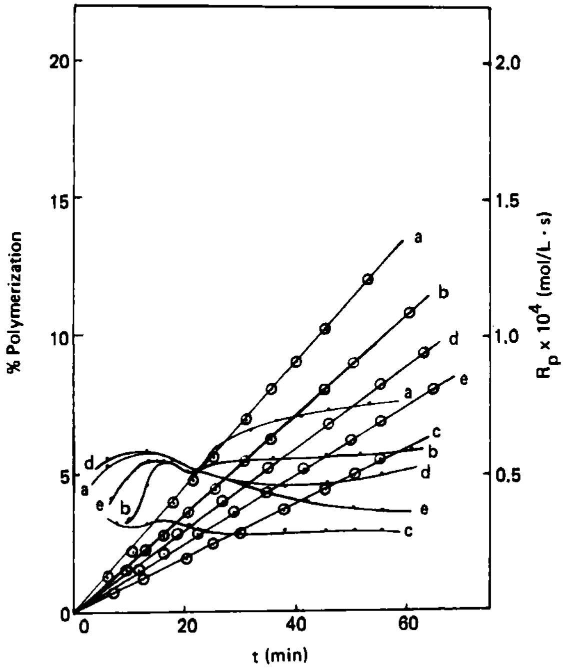

FIG. 4. Double plots of % polymerization and the rate of polymerization of MMA initiated by AIBN at 60°C and retarded by Ru(II) complexes at higher and lower concentrations than the critical range in DMSO. [MMA] = 1.872 mol/L, [AIBN] = 0.99×10^{-3} mol/L. (a) No added ruthenium complex, (b) [E] = 0.36×10^{-3} mol/L, (c) [E] = 0.09×10^{-3} mol/L, (d) [D] = 0.23×10^{-3} mol/L, (e) [D] = 0.04×10^{-3} mol/L.

than that without the added metal complex. From Table 1 it is evident that the rates of polymerization of MMA within the highest range of ratios of [AIBN] to [complex] are less than that with fixed [AIBN] alone.

As the concentration of metals complexes is increased, the rates of polymerization will gradually increase, reaching an optimum value at the optimum concentration of the metal complexes. From Table 1 it is clear that for the optimum concentration of each metal complex at the optimum ratio of [AIBN] to [complex], the rates of polymerization of MMA are higher than that with fixed [AIBN] alone, thus showing the accelerative effect of the complex.

Beyond the optimum concentration of the metal complexes, however, a part of each metal complex remains as such, thereby ac-

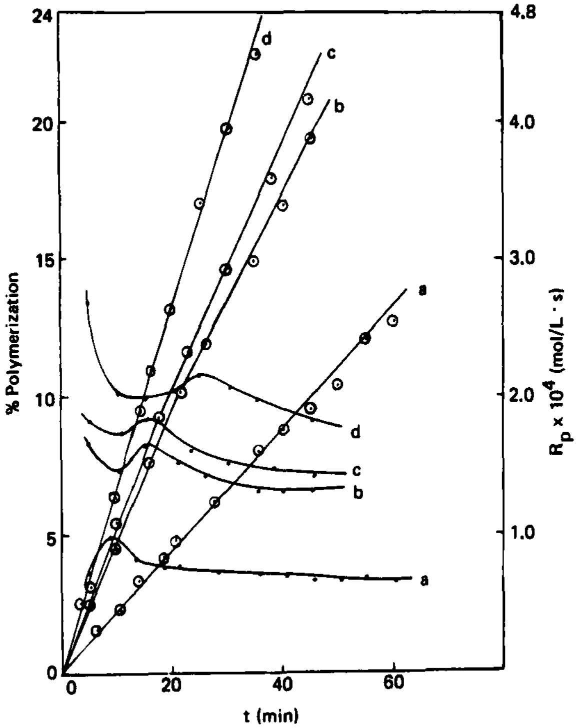

FIG. 5. Double plots of % polymerization and the rate of polymerization of MA initiated by AIBN at 60°C and accelerated by Rh(III) complexes at their critical concentrations in DMSO. [MA] = 1.888 mol/L, [AIBN] = 0.99 × 10^{-3} mol/L. (a) No added rhodium complex, (b) [A] = 0.01 × 10^{-3} mol/L, (c) [B] = 0.02 × 10^{-3} mol/L, (d) [C] = 0.32 × 10^{-3} mol/L.

counting for the fall of the rate curve. From Table 1 it is found that for higher concentrations of each metal complex when the ratios of [AIBN] to [complex] are less than the optimum ratio, the rates of polymerization of MMA are less than that with fixed [AIBN] alone.

Table 2 furnishes the results that the rates of polymerization of MA initiated by AIBN in the presence of A, B, C, D, and E at 60°C in DMSO within the optimum ratio of [AIBN] to [complex] are higher than that with fixed [AIBN] alone. In these ranges the metal complexes have an accelerative effect on the polymerization of MA.

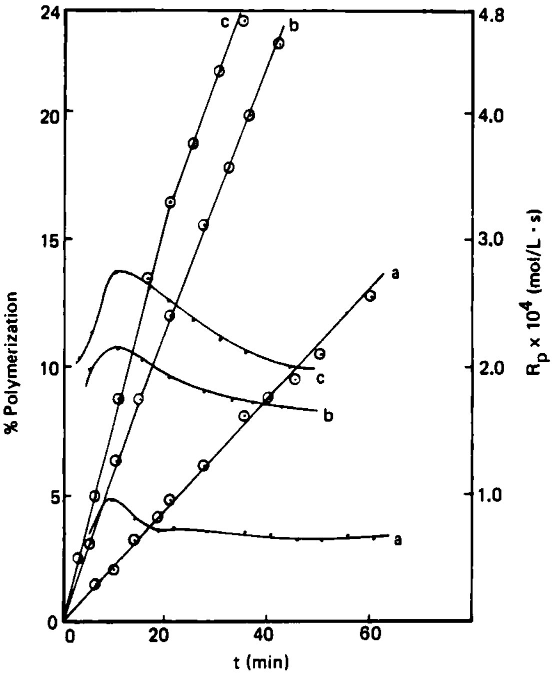

FIG. 6. Double plots of % polymerization and the rate of polymerization of MA initiated by AIBN at 60°C and accelerated by Ru(II) complexes at their critical concentrations in DMSO. [MA] = 1.888 mol/L, [AIBN] = 0.99×10^{-3} mol/L. (a) No added rughenium complex, (b) [D] = 0.05×10^{-3} mol/L, (c) [E] = 0.27×10^{-3} mol/L.

The accelerative effect of the metal complexes in the polymerization of MMA- and MA-initiated AIBN at 60°C is in the order C > B > A for Rh(III) complexes and E > D for Ru(II) complexes.

The bromo and chloro complexes of both Rh(III) and Ru(II) accelerate the polymerization of MMA- and MA-initiated AIBN at 60°C in a more efficient manner than the tetrafluoroborate complex of Rh(III) due to the nepheleuxetic effect [22].

TABLE 1. Rate of polymerization, R_p, and % Conversion of MMA Initiated by AIBN in the Presence of Rh(III) and Ru(II) Complexes in DMSO at 60°C[a]

Complex	Ratio	% Conversion	$R_p \times 10^4$ mol/L·s
-	-	10.5	0.73
A	50	5.2	0.36
A	99	11.5	0.82
A	165	4.6	0.31
B	16.5	6.4	0.44
B	33	12.6	0.84
B	165	7.2	0.52
C	2.3	8.2	0.58
C	3.2	16.2	1.10
C	33	6.3	0.43
D	4.3	6.9	0.48
D	16.5	15	1.06
D	25	5.8	0.40
E	2.75	8	0.56
E	6.2	16.8	1.12
E	11	4.2	0.30

[a] [AIBN] = 0.99×10^{-3} mol/L, ratio = [AIBN]/[complex], [A] = 0.06×10^{-4}-0.02×10^{-3} mol/L, [B] = 0.06×10^{-4}-0.06×10^{-3} mol/L, [C] = 0.03×10^{-3}-0.43×10^{-3} mol/L, [D] = 0.04×10^{-3}-0.23×10^{-3} mol/L, [E] = 0.09×10^{-3}-0.36×10^{-3} mol/L. [MMA] = 1.872 mol/L. Time = 45 min.

TABLE 2. Rate of Polymerization, R_p, and % Conversion of MA Initiated by AIBN in the Presence of Rh(III) and Ru(II) Complexes in DMSO at 60°C[a]

Complex	Ratio	% Conversion	$R_p \times 10^4$ mol/L·s
-	-	6.×	0.70
A	99	13.4	1.34
B	50	14.7	1.52
C	3.1	19.8	2.08
D	20	17.0	1.78
E	3.6	21.1	2.22

[a] [AIBN] = 0.99×10^{-3} mol/L, ratio = [AIBN]/[complex], [MA] = 1.888 mol/L, time = 30 min, [A] = 0.01×10^{-3} mol/L, [B] = 0.02×10^{-3} mol/L, [C] = 0.32×10^{-3} mol/L, [D] = 0.05×10^{-3} mol/L, [E] = 0.27×10^{-3} mol/L.

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REFERENCES

[1] N. Tokura, M. Matsuda, and F. Yazaki, Makromol. Chem., 42, 108 (1960).
[2] M. Matsuda, M. Iino, and N. Tokura, Ibid., 42, 232 (1963).
[3] W. I. Bengough and W. H. Fairservice, Trans. Faraday Soc., 61, 1206 (1965).
[4] H. C. Bamford and S. Brumby, Makromol. Chem., 134, 159 (1970).
[5] T. Fueno, H. Okamoto, T. Tsuruta, and J. Furukawa, J. Polym. Sci., 36, 407 (1959).
[6] P. D. Chetia and N. N. Dass, Eur. Polym. J., 12, 165 (1976).
[7] S. D. Baruah and N. N. Dass, J. Macromol. Sci.–Chem., A14(6), 841 (1980).
[8] S. S. Dixit, A. B. Despande, and L. S. Kapur, J. Polym. Sci., Part C, 31, 7 (1970).
[9] M. Ogewa and T. Ichiheshi, J. Polym. Sci., Part A-1, 9(6), 159 (1971).

[10] N. Kameda and N. Itagaki, Bull. Chem. Soc. Jpn., 46(8), 2597 (1973).
[11] C. H. Bamford, G. C. Eastmond, and W. R. Mattnan, Trans. Faraday Soc., 60, 1432 (1964).
[12] G. Odian, R. L. Kruse and J. H. T. Kho, J. Polym. Sci., Part A-1, 9, 91 (1971).
[13] M. H. George and P. F. Onyon, Trans. Faraday Soc., 59, 1390 (1963).
[14] S. R. Gupta and U. S. Nandi, J. Polym. Sci., Part A-1, 8, 1493 (1970).
[15] N. N. Dass and M. H. George, Ibid., 7, 269 (1969).
[16] Hovanska, J. Berton, and Z. Manasek, J. Polym. Sci., Polym. Chem. Ed., 10, 270 (1972).
[17] S. R. Sen and M. M. Singh, Indian J. Chem., 11, 497 (1973).
[18] N. D. Rubtsova, "Preparation and Studies of Complex Compounds of Rhodium with Dimethylsulphoxide," PhD Thesis, Leningrad Technological Institute, USSR, 1968.
[19] T. Bora and M. M. Singh, J. Inorg. Nucl. Chem., 38, 1815 (1976).
[20] T. Bora and M. M. Singh, Transition Metal Chem., 3, 27 (1978).
[21] A. Haeringer and G. Reiss, Eur. Polym. J., 14(2), 117 (1978).
[22] F. Basolo and R. G. Pearson, Mechanism of Inorganic Reaction, Wiley, New York, 1977, p. 112.

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