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Kinetics and mechanism of the reactions of a quasi-aromatic platinum(II) complex, [Pt(PnAO)–6H]^0, with formaldehyde

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Abstract—The kinetics and mechanism of the reaction of formaldehyde with a quasi-aromatic platinum(II) complex [Pt(PnAO)–6H]^0(AH), has been studied spectrophotometrically. The Pt,2N,3C quasi-aromatic heterocyclic ring in AH is highly reactive at the central-aromatic-carbon atom, C(12), to most aldehydes. Under neutral conditions in 1/3(*v*/*v*) MeOH–H$_2$O, the reaction scheme is as follows:

$$\mathrm{AH + CH_2O \xrightarrow{k_1} A{-}CH_2{-}OH \xrightarrow[+AH]{k_2} A{-}CH_2{-}A}$$

$$\mathrm{CH_2O + A{-}CH_2{-}A \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2A{-}CH_2{-}OH}$$

The substances AH, A—CH$_2$OH, and A—CH$_2$—A have been isolated and identified by ^{1}H NMR, IR. The kinetic data support the above reaction sequence. All reactions were second-order overall. The rate constants determined at 35.0°C were $k_1 = 5.94 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k_2 = 1.77$ dm^3 mol^{-1} s^{-1}, $k_3 = 0.120$ dm^3 mol^{-1} s^{-1}, $k_{-3} = 14.0$ dm^3 mol^{-1} s^{-1}. The activation parameters found for each step are as follows: $\Delta H_1^{\neq} = 56.0 \pm 2.8$ kJ mol^{-1}, $\Delta S_1^{\neq} = -105.8 \pm 9.1$ J K^{-1} mol^{-1}, $\Delta H_2^{\neq} = 45.0 \pm 2.9$ kJ mol^{-1}, $\Delta S_2^{\neq} = -94.4 \pm 9.2$ J K^{-1} mol^{-1}; $\Delta H_3^{\neq} = 52.9 \pm 1.8$ kJ mol^{-1}, $\Delta S_3^{\neq} = -91.0 \pm 5.7$ J K^{-1} mol^{-1}; $\Delta H_{-3}^{\neq} = 57.2 \pm 1.7$ kJ mol^{-1}, $\Delta S_{-3}^{\neq} = -37.6 \pm 5.4$ J K^{-1} mol^{-1}. The consequences of these reaction rate constants and their activation parameters are discussed. © 1997 Elsevier Science Ltd

Keywords: kinetics; quasi-aromatic complex; spectrophotometry.

The high reactivity at the C(12) position of AH (**A**) (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene) to electrophilic reagents was apparent by the ease of reaction with halogens to give A—X [1]. In our previous work, the kinetics and mechanism of the reaction between AH and aromatic aldehydes has recently been reported [2]. We also studied the kinetics and mechanism of the substituted reaction of Ni(II) analogue complex, [Ni(PnAO)–6H]^0, with formaldehyde and benzaldehydes [3,4]. The diazonium salt of sulfanilic acid produces a product with the properties expected and acid hydrolysis gives the same intensely purple colored substance which is also produced with malondialdehyde. Reaction with simple aldehydes such as formaldehyde and benzaldehyde has been shown to produce A—CH$_2$—A (**B**) and A—CHPh—A, respectively, rapidly and in high yields. Crystal structures of the aforementioned compounds have shown the basic platinum complexes to be intact and highly planar with a strong intramolecular hydrogen

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bond and to have little bond angle or distance differences between the molecules. It was of interest to know the kinetic nature of these reactions, the extent of side reactions, and what intermediates are involved. This work began with a spectrophotometric study of the AH-formaldehyde reaction in essentially neutral methanol-water $1/3(v/v)$ solution. Because of the relatively simple nature of the system and the lack of significant side reactions, we were successful in obtaining activation parameters for each step in the reaction.

EXPERIMENTAL

Materials

The ligand PnAO is reacted with K_2PtCl_4 in water by always keeping the ligand in excess. About 25% methanol as the solvent is used in order to raise the solubility of the ligand. This reaction takes several hours and must be gently warmed. After concentration by evaporation, concentrated potassium hydroxide is added slowly and with cooling to make the final solution 2 molar. $NaIO_3$ is then added in small quantities and stirred rapidly. It is best to heat it to about 50°C. $CHCl_3$ is used to extract the mixture, evaporated solvent, a dark brown solid is obtained. It is then recrystallized from water containing a small amount of acetonitrile to give $[Pt(PnAO)\text{-}6H]^0$. The formaldehyde solution used is a 35% aqueous solution (AR). It exists in water-solution primarily in the hydrated form, $CH_2(OH)_2$ [5]. CH_3OH (AR grade) was further purified by the Hartley–Baike method [6]. Deionized and redistilled water was used throughout.

Instruments

The UV–vis spectra were recorded on Shimadzu UV-240 spectrophotometer with a temperature controlled, ± 0.2°C, thermostatted cell. Matched quartz cells (1.00 cm) were used. The ^1H NMR spectra were obtained using a JEOL FX-90Q spectrometer. IR spectra were measured on Nicolet FT-IR 5DX spectrometer. Computations of the kinetic data were carried out with an AST-286 microcomputer using a nonweighted linear least-squares program. These rate constants were reproducible to $\pm 2\%$.

Experimental conditions

The experiments were carried out in unbuffered media at nearly neutral conditions (pH 5–6), because the reactant, AH, decomposes in acidic solution, and the solubilities of the reactant, the intermediate and the product complexes are low in pure water, a mixture of MeOH and water was used as solvent. Unless otherwise noted the reaction solvent consisted of $CH_3OH : H_2O = 1 : 3(v/v)$.

RESULTS

Identification of the intermediate and the product and the visible spectra

When equimolar amounts of AH and CH_2O are placed in a water solution, an orange crystalline precipitate gradually appears. By isolating the precipitate and analyzing it by IR, ^1H NMR, it was identified as A—CH_2—A. When A—CH_2—A was placed in CH_3OH—H_2O and treated with a large excess CH_2O, the UV spectral curves were measured. The absorption curves are shown in Fig. 1 and Fig. 2, respectively. After the reaction was completed, the product was removed by extraction with $CHCl_3$, to remove CH_2O, and the $CHCl_3$ was evaporated. A yellow solid substance was obtained, which by IR and ^1H NMR proved to be the ACH_2OH. The visible spectra of AH, ACH_2OH and A—CH_2—A are shown in Fig. 3. The extinction coefficients of ACH_2OH and A—CH_2—A at 399.5 nm were 823 and 6510, respectively. When solid ACH_2OH was added to the CH_3OH—H_2O solvent, it slowly disproportionated into ACH_2A and CH_2O. The visible spectrum is similar to that shown in Fig. 2 but the change is reversible. This indicates that the third step is a reversible reaction. When AH was reacted with a solution of ACH_2OH, the reaction proceeded relatively rapidly and ACH_2A was the only

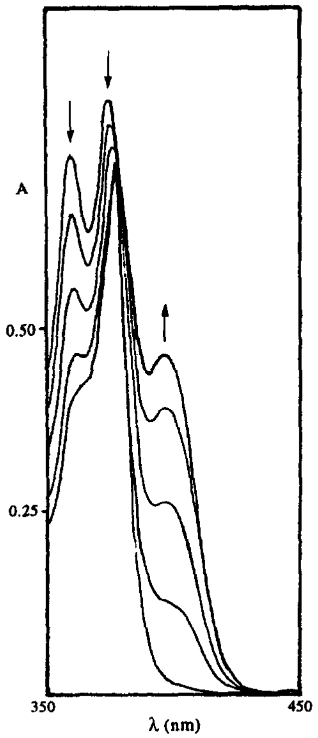
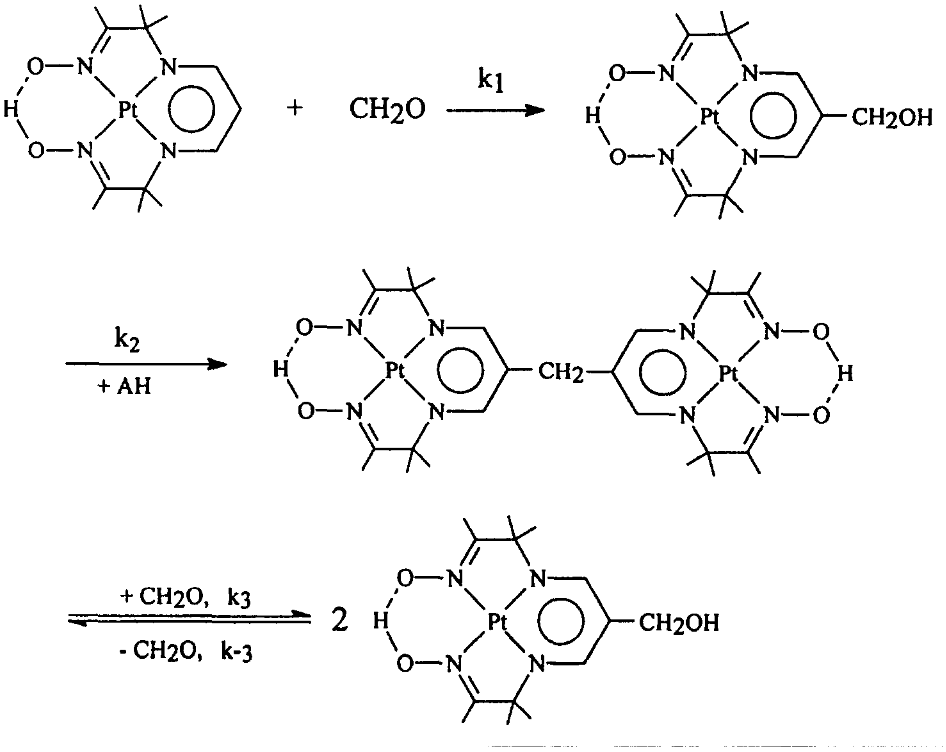


Fig. 1. Changes in the visible spectra during the reaction of equimolar AH and $CH_2(OH)_2$.

product. This proved that the second step is the reaction of AH with ACH_2OH and it is faster than the initial step.

Identification of reaction scheme

After a long series of semiquantitative spectral experiment, it was tentatively concluded that the reactions between CH_2O and AH are as follows:



The method of calculating the rate constants

All four of the reactions studied were shown to proceed through second-order kinetics. Some steps could be treated as pseudo first order, with an excess of one reagent. The first order equation is as follows:

$$\ln\left\{1+\frac{(\Delta\varepsilon[C]_0-A_\infty+A_0)(A_t-A_0)}{\Delta\varepsilon[C]_0(A_\infty-A_0)}\right\}$$

$$-\ln\left(\frac{A_\infty-A_t}{A_\infty-A_0}\right)=\left\{\frac{2\Delta\varepsilon[C]_0-A_\infty+A_0}{A_\infty-A_0}\right\}k_{obs}t$$

where $\Delta\varepsilon=(2\varepsilon_B-\varepsilon_C)$, ε_B, ε_C are the extinction coefficients of ACH_2OH, ACH_2A, respectively. A_0, A_∞ and A_t are absorbance at time 0, ∞, and t, respectively. k_{obs} is a pseudo-first-order rate constant. $k_{obs} = k_3[CH_2(OH)_2]_0 + \text{constant}$, where k_3 is the second-order rate constant. [C] is the concentration of ACH_2A. Changing $[CH_2(OH)_2]_0$ in a series of experiments and plotting k_{obs} against $[CH_2(OH)_2]_0$, allowed the calculation of the second-order rate constants were reproducible to about ±2%.

In some cases, it was impossible to use a large excess of one reactant in the system, so the second-order conditions were used. When the initial concentrations are not equal, the equation is:

$$\ln[(A_\infty-A_0)/(A_\infty-A_t) - (g_i/g_j)((A_t-A_0)(A_\infty-A_t))] = (g_jC_{i0}-g_iC_{j0})kt$$

where g_i, g_j and C_{i0}, C_{j0} are the stoichiometric coefficients and initial concentrations of reactant j, i. Conditions were set so $g_jC_{i0} \gg g_iC_{j0}$.

k_{-3} was calculated from the equilibrium constant K and k_3 using the expression $K = k_3/k_{-3}$. The equilibrium constant was experimentally determined using the equation

$$C_{ie} = C_{i0} + g_i(A_e - A_0)/Sg_j\varepsilon_j\,l, \quad K = \Pi_i C_{ie} g_i$$

where C_{ie} and C_{i0} are the concentrations at equilibrium and initial, respectively, and ε_i is the extinction coefficient of substance i. A_0 and A_e are absorbance of the system at initial and equilibrium concentration, respectively.

Reaction of CH_2O *with* ACH_2A, *in the absence of* AH, *in* $MeOH$–H_2O *gave the intermediate* ACH_2OH *at a rate comparable to the rate of the other reaction*

These facts establish that the reactions involved follow the reaction sequence suggested. Using the pro-

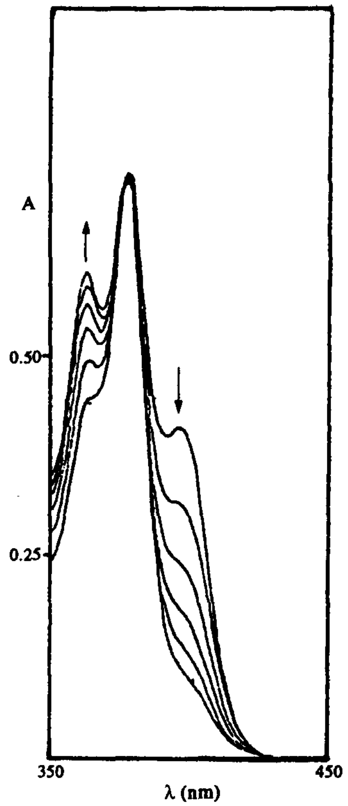


Fig. 2. Changes in the visible spectra during the reaction of ACH_2A with $CH_2(OH)_2$; $CH_2(OH)_2$ in large molar excess.

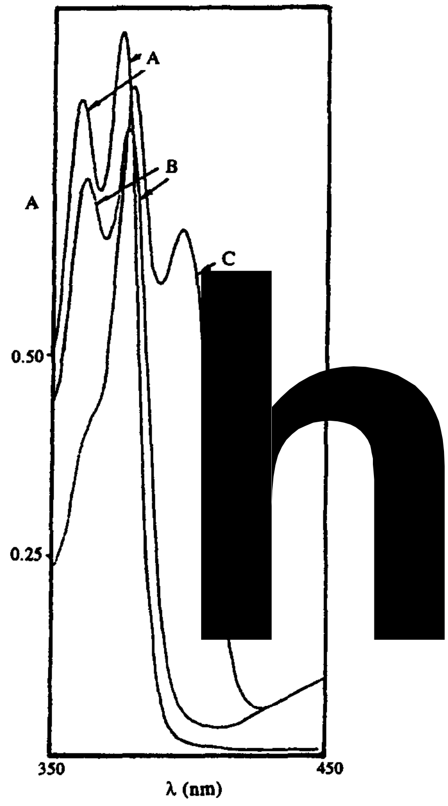


Fig. 3. Visible spectra of AH(A), ACH_2OH(B), and ACH_2A(C).

posed reaction scheme, we have determined the rate constants and the activation parameters of each step.

For all of the reactions of formaldehyde, it should be noted that CH_2O reacts with H_2O and CH_3OH to form $CH_2(OH)_2$, $CH_2(OH)OCH_3$, and $CH_2(OCH_3)_2$, [7] and three main equilibria exist in the solution [8].

$$H_2C{=}O + H_2O \rightleftarrows CH_2(OH)_2 \qquad K_1 = 41.04$$

$$H_2C{=}O + CH_3OH \rightleftarrows CH_2(OH)OCH_3 \qquad K_2 = 1310$$

$$H_2C{=}O + 2CH_3OH \rightleftarrows CH_2(OCH_3)_2 + H_2O \qquad K_3 = 183$$

The experimental rate data showed that when the concentration of CH_3OH was increased the rate of the reactions became slower. Therefore we presume that $CH_2(OH)_2$ reacts more rapidly with AH, than does $CH_2(OH)OCH_3$ or $CH_2(OCH_3)_2$. From the equilibrium constants, under the conditions of the experiment, we calculate that

$$[CH_2(OH)_2] = 0.170[CH_2O]_T$$

where $[CH_2O]_T$ is the total concentration of CH_2O. The concentration of free formaldehyde was very small ($0.00005[CH_2O]_T$). We have no reliable estimate of the relative reactivities of each of the formaldehyde species, however, it is clear that methylation of CH_2O lowers the rate of reaction. The value of k_3 is proportional to F, the fraction of hydrated aldehyde form, $CH_2(OH)_2$ (see Table 1). So we have calculated the rate constants and equilibrium constants as if only the hydrated form, $CH_2(OH)_2$, was reactive.

k_1 was determined by having a slight excess of CH_2O in the solution. At these concentrations the product was almost entirely ACH_2A. Spectrophotometric measurement at 399.5 nm was employed together with the measured extinction coefficients (Table 2) to give the rate parameters. Since $k_2 \gg k_1$, under the experimental conditions employed, the third step of the reaction could be ignored and the steady-state method could be applied:

$$d[ACH_2OH]/dt = k_1[AH][ACH_2(OH)_2] - k_2[AH][ACH_2OH] = 0,$$

$$d[ACH_2A]/dt = k_2[AH][ACH_2OH].$$

Therefore $d[ACH_2A]/dt = k_1[AH][ACH_2(OH)_2]$.

Table 1. k_{obs} of the positive reaction of the third step, at different solvent conditions

$MeOH:H_2O(V:V)$	1:1	1:2	1:3	1:4
$F = [CH_2(OH)_2]/[CH_2O]_T$	0.0616	0.119	0.170	0.215
k_{obs} (S^{-1})	0.431	2.59	4.80	6.72

Table 2. Extinction Coefficients of AH, ACH_2OH and ACH_2A (cm^{-1} M^{-1})

Temp (K)	303.2	308.2	313.2	318.2	323.2	328.2
AH (376.4 nm)	3674	3656	3632	3609	3580	3563
ACH_2OH (399.5 nm)	817	823	829	837	844	853
ACH_2A (399.5 nm)	6482	6510	6542	6586	6643	6730

Because the overall reaction was

$$2AH + CH_2O \rightarrow ACH_2A + H_2O,$$

g_i has a value of 2 when the second-order equation was utilized.

The value of k_2 was determined by following the reaction of AH with ACH_2OH. Again the wavelength 399.5 nm was used to follow the reaction. The reaction was begun by injection of a small volume of AH solution into a dilute solution of ACH_2OH. The latter was prepared by reaction of excess CH_2O with AH, extracted with $CHCl_3$, and purification. The kinetic data were treated in accordance with the second-order reaction equation for similar but unequal concentrations of the two reactants.

By observation of the formation of ACH_2OH upon injection of a large excess amount of CH_2O into a solution of ACH_2A, the rate constant k_3, was determined. Usually the pseudo-first-order equation was applied to data taken at 399.5 nm. Although CH_2O is in large excess, a more accurate equation (k_3) in which the reversible reaction was taken into account. Treatment of the data only concerning positive reaction (k'_3) gave the smaller results (in the right column), the different results are listed in Table 3.

Four experiments were performed at each temperature when the pseudo-first-order method (accurate equation) was used, in which the initial concentration of CH_2O was changed. The result of k_{obs} versus $[CH_2(OH)_2]$ are shown in Table 4.

k_{-3} was calculated from k_3 and the equilibrium constant, K. Values for the latter were determined at a series of temperatures.

	308.2 K	313.2 K	318.2 K	323.2 K
$K \times 10^3$	8.56	8.37	8.15	7.92

Table 5 shown the rate constants for each step at different temperatures. The correlation coefficient was >0.999 for all first- or second-order equation fits to the data. The activation parameters calculated for each step are listed in Table 6.

Table 3. The rate constants of the third step, at different treatments

Temp. (K)	k_3(l mol^{-1} s^{-1})	k'_3 (l mol^{-1} s^{-1})
308.2	0.120	0.0761
313.2	0.170	0.105
318.2	0.246	0.148
323.2	0.324	0.186

Table 4. k_{obs} as a function of temperature and formaldehyde concentration

Temp. (K)	308.2	313.2	318.2	323.2
$[CH_2(OH)_2] \times 10^3$ (mol/l)	$k_{obs} \times 10^3$ (s^{-1})			
3.818	0.496	0.661	0.895	1.14
9.545	1.25	1.84	2.25	3.14
19.09	2.65	3.20	4.80	6.61
28.62	3.61	4.68	7.31	9.59
38.18	4.61	6.03	9.38	12.2
k_3 (l mol^{-1} s^{-1})[a]	0.120	0.170	0.246	0.324

[a] $k_{obs} = k_3[CH_2(OH)_2]$ + constant. From a graph of k_{obs} *vs* $[CH_2(OH)_2]$, $R > 0.999$

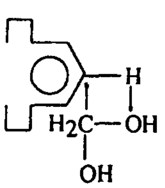
Table 5. Rate constants as a function of temperature[a]

Temp. (K)	308.2	313.2	318.2	323.2
$k_1 \times 10^3$	5.94	9.20	12.6	17.4
k_2	1.77	2.40	3.36	4.12
k_3	0.120	0.170	0.246	0.324
k_{-3}	14.0	20.3	30.2	41.4

[a] The units for k are l mol^{-1} s^{-1}.

DISCUSSION

The systems were well behaved in a kinetic sense and there was no evidence suggesting significant side reactions. Because of the known sensitivity of the reaction rates to acid, we were concerned that small differences in acidity from sample to sample might decrease the reproducibility. This did not seem to be important however as the reproducibility was excellent. On a broad basis it appears remarkable that all of the reactions studied are so facile at the moderate temperature and concentration conditions used. This must be a reflection of the high reactivity of the C(12) position and that probably results from the relatively high partial negative charge on that atom. We suggest that there is a common, similar four-membered ring transition state in each step. The transition states suggested are shown in Scheme 1.



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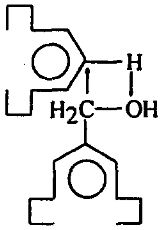

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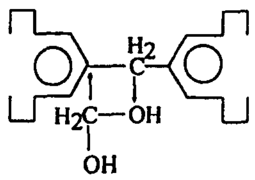

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Table 6. Kinetic activation parameters for each step

Step	1	2	3	−3
$\Delta H^{\neq}$ (KJ/mol)	56.0±2.8	45.0±2.9	52.9±1.8	57.2±1.7
$\Delta S^{\neq}$ (J/K/mol)	−105.8±9.1	−94.4±9.2	−91.0±5.7	−37.6±5.4
r	0.997	0.996	0.999	0.999

The values of activation enthalpy of all three steps are negative ones implying that there is a closer structure in transition state. This is consistent with the hypothesis of four-membered ring transition state. The first-step reaction is a cooperative reaction, the break of C—H bond and the formation of C—C bond almost synchronize. The second step has a smaller $\Delta H^{\neq}$, it is considered that at transition state, C—O bond has partially been broken, *p*-orbit of bridge carbon atom connecting two quasi-aromatic heterocyclic ring is partially contributed to the π conjugate system. So, the energy of transition state decreases obviously. The third step is an opposite reaction. In terms of the principle of microscopic reversibility, there is a same transition state either positive reaction or reversible one. On the basis of the break of C—O bond and C—C bond, the reaction occurs in a different direction. It is known that the bond energy of Ph—C is 418 kJ mol^{-1}, that of C—O in $Ph\text{-}CH_2OH$ is 326 kJ mol^{-1} [9]. Thus, the break of C—O bond is easier, there is much more tendency towards the reversible reaction.

This work has shown that the reaction of AH with the simplest aldehyde is free from side reaction and proceeds at moderate rates under ordinary conditions. Using the information obtained, one can predict conditions under which either of the products can be obtained in nearly theoretical yield in solution.

REFERENCES

1. Vassian, E. G. and Murmann, R. K., *Coord. Chem. Revs.*, 1990, **105**, 1.
2. Zhang, Y.-M., Lin, H.-K., Chen, Y.-T. and Murmann, R. K., *Polyhedron*, 1995, **14**, 1083.
3. Song, B., Zhang, Q.-Y., Chen, Y.-T. and Murmann, R. K., *Inorg. Chem.*, 1992, **31**, 2314.
4. Song, B., Zhang, Q.-Y., Chen, Y.-T. and Murmann, R. K., *J. Indian Chem. Soc.*, 1992, **69**, 420.
5. Zhang, Y.-M., Ph.D. Thesis Nankai University, Tianjin, P.R. China, 1993.
6. Perrinand, D. D. and Armarego, W. L. F., *Purification of Laboratory Chemicals*, p. 320–321 Pergamon Press, Oxford (1980).
7. Carey, F. A. and Sundberg, R. J., *Advanced Organic Chemistry*; Part A, p. 264. Plenum, New York (1977).
8. Guthie, J. P., *Can. J. Chem.*, 1975, **53**, 898.
9. Yao, Y.-B., Xie, T. and Gao, Y.-M., *Handbook of Physicochemistry*, p. 118. Shanghai Science and Technology Publishing House, P.R. China (1985).