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Thermal Stability of Substituted Pyridine Adducts of Bis(acetylacetonato)-oxovanadium(IV) in Solid State

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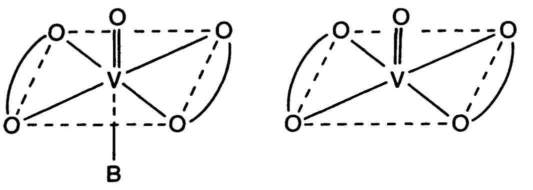
The kinetic of the elimination reaction of axial ligand B in [VO(acac)$_2$B] complexes (Hacac=acetylacetone; B=pyridine, its derivatives, and ammonia) was studied in solid state by the Coats-Redfern method. The frequency factor and activation energy were determined, from which the activation free energy (ΔG^*) was calculated. The ΔG^* values varied with the nature of pyridine derivatives in the range of 99—109 kJ mol^{-1}. The insight into ΔG^* values suggests that the kinetic stability of vanadium-substituted pyridine bond is influenced by both the basicity (pK_a) and heat of sublimation ($\Delta H_{(sub)}$) of the axial ligand. Furthermore, the E' values which appear to reflect coordination ability of base B were determined by reflectance spectra of the complexes. The E' value was found to increase linearly with the increase in pK_a and $\Delta H_{(sub)}$ of the axial ligand.

The stability and reactivity of metal complexes have generally been discussed on the basis of kinetic and thermodynamic data of substitution reactions in solution. Since the reactant and product are naturally solvated with medium molecules, the kinetic and thermodynamic data have to be corrected for interaction between reactants and solvent. On the other hand, the thermal reaction in solid state will directly provide information concerning not only the strength of metal-ligand bond,[1] but also the formation of intermediate products.[2] We studied previously the thermal aniline elimination reaction of [Co(Hbhpn)A$_2$]X$_2$[3] and [Ni(acac)$_2$A$_2$][4] complexes, where H$_2$bhpn: *N,N'*-bis(2-hydroxyimino-1-methylpropylidene)-1,3-propanediamine, A: aniline or its derivatives, X: Cl$^-$, Br$^-$, or I$^-$ ion, and Hacac: acetylacetone. The results revealed that the kinetic stability of metal-substituted aniline bond for these complexes mainly depends on the pK_a and the heat of sublimation of aniline and its derivatives; a linear correlation between the experimental ΔG^* of the elimination reaction and pK_a values of the aniline derivatives was observed except the complexes with *p*-chloroaniline and *p*-bromoaniline having larger heat of sublimation than other aniline derivatives.

In the present work, thermal analysis has been carried out on the thermal elimination reaction of a series of adduct complexes, mono(substituted pyridine)bis(acetylacetonato)oxovanadium(IV) shown in Fig. 1-[I], (abbreviated as [VO(acac)$_2$B], B=pyridine, its derivatives,[5] and ammonia) to elucidate the influence of heat of sublimation of axial ligand on thermal stability of these complexes. In the thermal analysis of [VO(acac)$_2$B] complexes, it was confirmed that these complexes endothermically dissociate the axial ligand to give green [VO(acac)$_2$] complex shown in Fig. 1-[II]. The activation free energy of the elimination reaction will be briefly discussed in connection with the nature of vanadium-substituted pyridine bond.



[I]
[VO(acac)$_2$B]

[II]
[VO(acac)$_2$]

Fig. 1. [VO(acac)$_2$B][I] and [VO(acac)$_2$][II].

Experimental

Materials. The parent complex [VO(acac)$_2$] was prepared as described in the literature.[6] Its pyridine adducts, [VO(acac)$_2$B], were prepared as described in the literature,[7] except those with 4-CN-py and 3-CN-py. Because 4-CN-py and 3-CN-py are slightly soluble in ether, they were first dissolved in a minimum quantity of water and then added to [VO(acac)$_2$] in ether. The mixture was refluxed for about 1 h and solid residue was filtered off as the complex desired. The ammonia adduct, [VO(acac)$_2$(NH$_3$)], was prepared by the method of Claunch et al.[8] These adducts were identified by elemental analyses and IR spectroscopy.

Analytical Data for [VO(acac)$_2$B]. Found: C, 52.37; H, 5.45; N, 4.14; V, 14.38%. Calcd for [VO(acac)$_2$(py)]: C, 52.33; H, 5.57; N, 4.07; V, 14.80%. Found: C, 52.38; H, 5.74; N, 3.90; V, 13.90%. Calcd for [VO(acac)$_2$(4-CH$_3$-py)]; C, 53.68; H, 5.92; N, 3.91; V, 14.22%. Found: C, 54.58; H, 6.14; N, 3.92; V, 13.33%. Calcd for [VO(acac)$_2$(4-C$_2$H$_5$-py)]: C, 54.84; H, 6.24; N, 3.76; V, 13.68%. Found: C, 48.92; H, 4.76; N, 6.93; V, 13.50%. Calcd for [VO(acac)$_2$(4-CN-py)]: C, 52.04; H, 4.92; N, 7.59; V, 13.79%. Found: C, 49.53; H, 4.78; N, 7.03; V, 13.60%. Calcd for [VO(acac)$_2$(3-CN-py)]: C, 52.04; H, 4.92; N, 7.59; V, 13.79%. Found: C, 40.96; H, 4.09; N, 3.20; V, 11.95%. Calcd for [VO(acac)$_2$(3-Br-py)]: C, 42.58; H, 4.29; N, 3.31; V, 12.04%. Found: C, 41.68; H, 5.96; N, 4.88; V, 17.83%. Calcd for [VO(acac)$_2$(NH$_3$)]: C, 42.57; H, 6.07; N, 4.96; V, 18.04%.

Measurements. The TG and DSC curves were recorded in a flowing nitrogen atmosphere of 100 cm^3 min^{-1} at a heating rate of 10 °C min^{-1} on a Rigaku Denki 8002 thermal analyzer. α-Al$_2$O$_3$ was used as reference material. The heat of the elimination reaction was determined by measuring the DSC peak area. The instrument was calibrated against the heat of

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transition of potassium nitrate and silver nitrate. The kinetic analysis under nonisothermal conditions was carried out on the TG curves recorded at a heating rate of 1 °C min^{-1} for 8—9 mg of sample. The particle size of samples for the measurements was under 100 mesh.

Reflectance spectra of the complexes in the visible region were recorded on a Hitachi Model 340 spectrophotometer equipped with a R-10A integrating sphere, using MgO as the reference substance.

Results and Discussion

Thermal Analysis. The TG and DSC curves for [VO(acac)$_2$B] complexes are shown in Figs. 2-(a) and 2-(b). The DSC data are summarized in Table 1.

As shown in Fig. 2-(a), in the case of [VO(acac)$_2$(py)] complex, the weight-loss (21.3%) on the TG curve in the temperature range of 83—142 °C, can be attributed to the elimination of one mole of pyridine (22.9%). An endothermic phenomenon was observed on the DSC curve corresponding to this weight decrease. For other complexes, the decrease in weight and endothermic phenomenon corresponding to the ligand elimination were similarly observed in the range of 90—170 °C; the weight loss was 25.8% (Calcd 26.0%) for [VO(acac)$_2$(4-CH$_3$-py)], 29.0%(28.8%) for [VO(acac)$_2$(4-C$_2$H$_5$-py)], 26.6%(28.2%) for [VO(acac)$_2$(4-CN-py)], 27.1%(28.2%) for [VO(acac)$_2$(3-CN-py)], 36.5%(37.3%) for [VO(acac)$_2$-(3-Br-py)], and 5.8%(6.0%) for [VO(acac)$_2$(NH$_3$)].

The infrared spectra of the decomposition products were measured at appropriate steps of the reaction process appearing in the TG and DSC curves. As mentioned above, [VO(acac)$_2$(py)] loses one mole of pyridine at about 142 °C. The IR spectrum of [VO-(acac)$_2$(py)] at 142 °C does not give the bands of pyridine ring[9,10] at 1444, 1218, and 711 cm^{-1} at room temperature. However, substantial change in the bands at 1523, 1371, and 934 cm^{-1} due to the coordinated acetylacetonate[10] were not observed, and the spectrum of this decomposition product was found to be the same as that of [VO(acac)$_2$]. Analyses of the infrared spectra of thermal decomposition products suggested that the thermal decomposition of complexes was elimination of pyridine derivatives from [VO(acac)$_2$B] as expressed below:

$$[\mathrm{VO(acac)_2B}] \xrightarrow[\text{endo.}]{} [\mathrm{VO(acac)_2}] + \mathrm{B}\uparrow.$$

As seen in Table 1, the enthalpy changes (ΔH) for [VO(acac)$_2$(py)] and [VO(acac)$_2$(4-CH$_3$-py)] were 69.4 and 81.4 kJ mol^{-1}, respectively, which are comparable

Table 1. DSC Data of [VO(acac)$_2$B] Complexes

Base	pK_a	$\Delta H_{(\mathrm{sub})}$$^{a)}$	(K)$^{b)}$	$\Delta H^{c)}$
		kJ mol^{-1}		kJ mol^{-1}
py	5.25	47.8	404	69.4
4-CH$_3$-py	6.02	56.9	421	81.4
4-C$_2$H$_5$-py	6.17	54.0**	425	73.2
4-CN-py	1.90	75.6*	399	65.5
3-CN-py	2.28	79.0*	391	68.2
3-Br-py	2.84	59.4*	402	74.7
NH$_3$	9.26	29.0	370	51.3

a) $\Delta H_{(\mathrm{sub})}$$^{a)}$, enthalpy of sublimation for pyridine derivatives. *, $\Delta H_{(\mathrm{sub})}$ values determined by DSC measurement; **, enthalpy of vaporization. b) DSC maximum peak temperature. c) ΔH, heat of reaction.

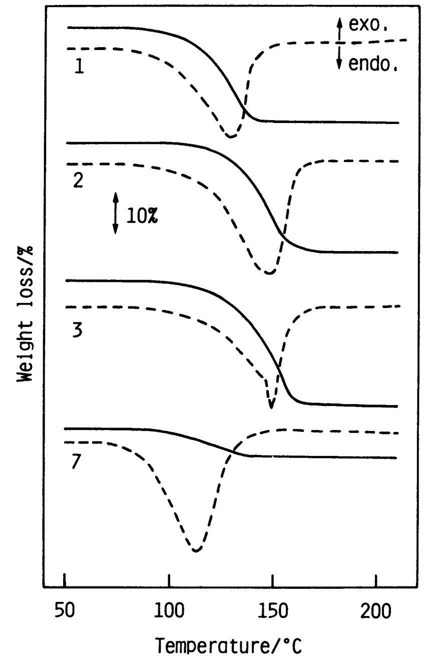

Fig. 2a. TG (—) and DSC (----) curves of [VO-(acac)$_2$B] complexes; heating rate 10 °C min^{-1}. B= 1: py, 2: 4-CH$_3$-py, 3: 4-C$_2$H$_5$-py, 7: NH$_3$.

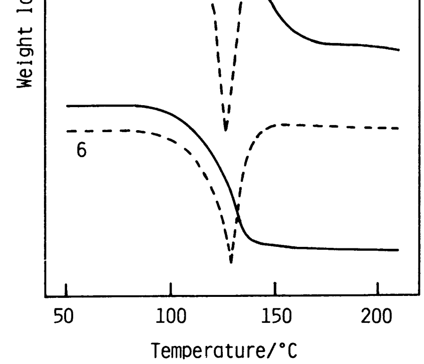

Fig. 2b. TG (—) and DSC (----) curves of [VO-(acac)$_2$B] complexes; heating rate 10 °C min^{-1}. B= 4: 4-CN-py, 5: 3-CN-py, 6: 3-Br-py.

to those of the thermal elimination of [VO(dbm)$_2$(py)] (71.5 kJ mol^{-1}) and [VO(dbm)$_2$(4-CH$_3$-py)] (93.5 kJ mol^{-1}), where dbm is dibenzoylmethane.[11]

Kinetic Stability. The thermal stability of complexes has often been discussed in terms of the initiation temperature of decomposition reaction or the DSC maximum peak temperature. Since the temperature observed on the thermoanalytical curves is affected by the experimental conditions and the reaction mechanism, the thermal stability concerning the bond strength of metal-ligand linkage should be discussed by using a kinetic parameter rather than the initiation temperature.

Hence the kinetic analysis was carried out in order to ascertain the kinetic feature of [VO(acac)$_2$B] complexes. The rate plot under nonisothermal conditions was obtained by use of the following Eq. 1 proposed by Coats and Redfern:[12]

$$\left.\begin{aligned}&(\text{when } n = 1)\ \log\left\{\frac{-\log(1-\alpha)}{2.303T^2}\right\}\\[2ex]&(\text{when } n \neq 1)\ \log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\}\end{aligned}\right\}$$
$$= \log\frac{AR}{\phi E_a}\left(1-\frac{2RT}{E_a}\right)-\frac{E_a}{2.303RT}, \qquad (1)$$

where E_a is activation energy; A, frequency factor; α, molar fraction of complex decomposed; T, absolute temperature; R, gas constant; ϕ, heating rate; and n, order of reaction. The plot of $\log\{-\log(1-\alpha)/(2.303T^2)\}$ against $1/T$ when $n=1$ gives a straight line, as shown in Fig. 3. The E_a and A values were calculated from the slopes and intercepts of these straight lines, respectively. The activation enthalpy $\Delta H^{\ddagger}$ was calculated from $\Delta H^{\ddagger}=E_a-RT$, while the activation entropy $\Delta S^{\ddagger}$ was obtained from $\Delta S^{\ddagger}=R[\ln(Ah/kT)-1]$, where k is the Boltzman constant, and h, the Planck constant, assuming the transmission coefficient to be 1. In addition, in order to disclose the contribution of the entropic term to the reaction, the activation free energy $\Delta G^{\ddagger}$ was calculated by the relation, $\Delta G^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger}$. The kinetic characteristics are tabulated in Table 2.

Since the thermal reaction of [VO(acac)$_2$B] complexes belongs to the elimination reaction of base B, the kinetic stability of the vanadium-base bond was expected to vary with the basicity of the bases. However, as seen in Table 2, in spite of pK_a values of the bases varying in wide range of 1.90—9.26, the activation free energy $\Delta G^{\ddagger}$ change in narrow range of 99—109 kJ mol^{-1}. On the other hand, when pyridine or its derivative forms a complex with a transition metal, the bonding consists of σ and π interactions between metal and substituted pyridine. It has been reported that in the thermal decomposition of [Ag(B)$_2$NO$_3$][13] and [Co(salen)(B)][14] (salen=N,N'-ethylenebis(salicylideneaminato)dianion), the complex with 4-CN-py has unusually large E_a value in comparison with those of py, 3-CH$_3$-py, and 3-CN-py complexes. The large E_a value observed in 4-CN-py complex has been interpreted by taking into account a significant contribution of metal–base π-back-bonding to the bond stability. In the present complexes, [VO(acac)$_2$(4-CN-py)] was also expected to be more stable than [VO(acac)$_2$(3-CN-py)], [VO(acac)$_2$(3-Br-py)], and [VO(acac)$_2$(py)]. However, no remarkable difference in $\Delta G^{\ddagger}$ values among these complexes was observed.

These facts suggest that the thermal stability of

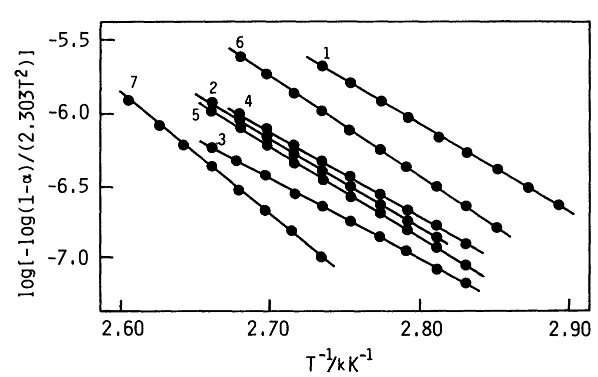

Fig. 3. Plots by the Coats-Redfern method for pyridine elimination of [VO(acac)$_2$B] complexes. B= 1: py, 2: 4-CH$_3$-py, 3: 4-C$_2$H$_5$-py, 4: 4-CN-py, 5: 3-CN-py, 6: 3-Br-py, 7: NH$_3$.

Table 2. Kinetic Data of Pyridine Derivatives for the Elimination Reactions of [VO(acac)$_2$B] Complexes

Base	E_a / kJ mol^{-1}	$\log(A/\text{s}^{-1})$	$\Delta H^{\ddagger}$(400 K) / kJ mol^{-1}	$\Delta S^{\ddagger}$(400 K) / J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$(400 K) / kJ mol^{-1}
py	123±9	16.1±1.2	120±9	52±12	99±2
4-CH$_3$-py	123±10	15.3±1.4	119±10	37±15	105±2
4-C$_2$H$_5$-py	103±9	12.3±1.2	100±9	−20±10	108±0.2
4-CN-py	113±4	13.9±0.6	110±4	11±6	105±0.2
3-CN-py	119±0.6	14.9±0.1	116±0.3	29±0.4	104±0.4
3-Br-py	126±7	16.2±1.1	123±7	54±7	101±0.7
NH$_3$	157±1	19.2±0.5	153±1	110±2	109±0.5

E_a, activation energy; A, frequency factor; $\Delta H^{\ddagger}$, activation enthalpy; $\Delta S^{\ddagger}$, activation entropy; $\Delta G^{\ddagger}$, activation free energy.

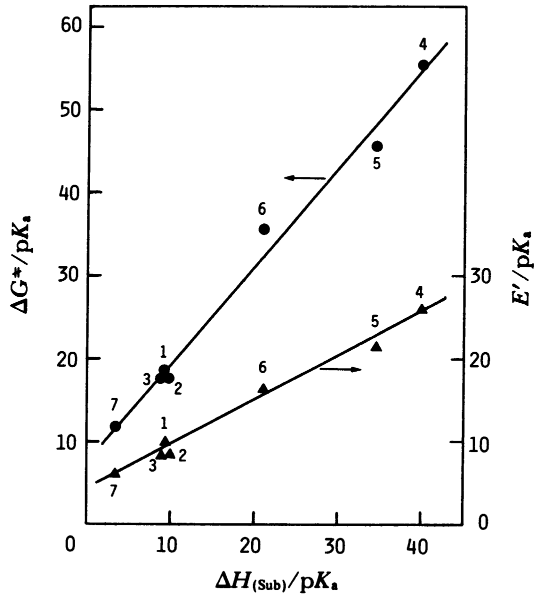

Fig. 4. Plots (—●—●—) of $\Delta G^{*}/pK_a$ against $\Delta H_{(sub)}/pK_a$, plots (—▲—▲—) of E'/pK_a against $\Delta H_{(sub)}/pK_a$. B=1: py, 2: 4-CH_3-py, 3: 4-C_2H_5-py, 4: 4-CN-py, 5: 3-CN-py, 6: 3-Br-py, 7: NH_3.

complexes is affected by various interactions, including the metal–base σ-bond, π-bond, and steric interaction.

As mentioned before, our previous studies[3,4] for the thermal reactions of [$Ni(acac)_2A_2$] and [Co(Hbhpn)-A_2]X_2 complexes revealed that the thermal stability of these complexes is influenced by the heat of sublimation of base A itself as well as basicity of the base. As for [$VO(acac)_2B$], it is assumed that the thermal stability may be influenced by the thermal properties such as the heat of fusion and vaporization in the following equation:

$$\Delta G^{*} = \alpha pK_a + \beta \Delta H_{(sub)}, \qquad (2)$$

where α and β are constants determined by the reaction system, and $\Delta H_{(sub)}$ is the heat of sublimation (sum of heat of fusion and vaporization). Dividing both sides of Eq. 2 by pK_a yields Eq. 2′:

$$\Delta G^{*}/pK_a = \alpha + \beta \Delta H_{(sub)}/pK_a, \qquad (2')$$

If the above assumption is adequate, a straight line with slope β will be obtained. As shown in Fig. 4, the plot between $\Delta G^{*}/pK_a$ and $\Delta H_{(sub)}/pK_a$ indicates that $\Delta G^{*}/pK_a$ and $\Delta H_{(sub)}/pK_a$ bear a linear correlation. This result suggests that the thermal stability of [$VO(acac)_2B$] complexes investigated here depends mainly on the basicity and the heat of sublimation of base B.

Reflectance Spectra. The reflectance spectral data for [$VO(acac)_2B$] are summarized in Table 3. The lowest energy band can be assigned to $^2E \leftarrow {}^2B_2$ transition and the second band to $^2B_1 \leftarrow {}^2B_2$ transition (10 Dq). Selbin et al.[15] reported that a parameter D_{12}, the difference in positions between the first and the second band maxima, is more sensitive than 10 Dq in the coordination ability of ligands. Then, the D_{12} values for these complexes were determined and converted to energy E'(kJ mol^{-1}) as shown in the 5th column of Table 3.

Table 3. Reflectance Spectral Data of [$VO(acac)_2B$] Complexes in Solid State

Base	Band 1	Band 2	D_{12}	E'
	cm^{-1}	cm^{-1}	cm^{-1}	kJ mol^{-1}
py	12890	17300	4410	52.7
py[15]	(13000)	(17390)	(4390)	
4-CH_3-py	13000	17240	4240	50.7
4-C_2H_5-py	12990	17180	4190	50.1
4-CN-py	12950	17060	4110	49.1
3-CN-py	13120	17180	4150	49.6
3-Br-py	13370	17270	3900	46.6
NH_3	12630	17180	4550	55.4

E', Calculated from D_{12} values.

The tendency in E' value for each complex is similar to that for ΔG^{*} value as described above. In other words, no dependence of E' on basicity of the bases was observable. Therefore, in this case, Eq. 2″ was assumed:

$$E'/pK_a = \alpha' + \beta' \Delta H_{(sub)}/pK_a, \qquad (2'')$$

where α' and β' are constants. As seen in Fig. 4, a linear correlation was observed between E'/pK_a and $\Delta H_{(sub)}/pK_a$. These results support the assumption that the stability in connection with the strength of metal–ligand bond is affected by the electron donating power and the heat of sublimation of base B.

Variations in the values of ΔG^{*} and E' with different ligand can be attributed to changes in the strength of metal–ligand σ-bond, the magnitude of metal–ligand π-bond, and the steric interaction. The basicity of ligand will relate to the strength of σ-bond. However, it is difficult to evaluate the degree of the character of π-bond and steric interaction. Although the heat of fusion and vaporization of ligand does not necessarily reflect the character of π-bond and steric interaction, both the characters may have correlation to the thermal property through hydrogen bond and van der Waals force. Therefore, the thermal properties such as heat of fusion and vaporization were used for explaining the difference in ΔG^{*} and E' values. Thus, the thermal stability of [$VO(acac)_2B$] complexes seems to depend mainly on the pK_a and $\Delta H_{(sub)}$ of base B. A similar observation has been reported for dehydration–anation reaction of [$Cu(en)_2(H_2O)_2$]X_2[16] (en=ethylenediamine, X=Cl^-, Br^- ion) and $CoCl_2 \cdot nH_2O$ (n=1—6)[17] to discuss the influence of intermolecular hydrogen bonds on the activation energy and the enthalpy change of dehydration reaction.

References

1) G. Beech and C. T. Mortimer, *J. Chem. Soc. A*, **1967**,

1115; J. C. Van Dam, G. Hakvoort, and J. Reedijk, *J. Therm. Anal.*, **20**, 3 (1981); K. Boguslawska and A. Cygański, *J. Therm. Anal.*, **24**, 15 (1982).

2) J. G. Murgulescu, E. Segal, and D. Fătu, *J. Inorg. Nucl. Chem.*, **27**, 2677 (1965); P. Pfeiffer and Fr. Tappermann, *Z. Anorg. Allg. Chem.*, **214**, 273 (1933); W. W. Wendlandt and C. H. Stembridge, *J. Inorg. Nucl. Chem.*, **27**, 575 (1965).

3) Y. Shibutani and K. Shinra, *Nippon Kagaku Kaishi*, **1988**, 143.

4) Y. Shibutani, H. Tachikawa, and K. Shinra, *Nippon Kagaku Kaishi*, **1988**, 1816.

5) The following abbreviations are used: py, pyridine; 4-CH$_3$-py, 4-methylpyridine; 4-C$_2$H$_5$-py, 4-ethylpyridine, 4-CN-py, 4-cyanopyridine; 3-CN-py, 3-cyanopyridine, 3-Br-py, 3-bromopyridine.

6) R. A. Rowe and M. M. Jones, *Inorg. Synth.*, **5**, 115 (1957).

7) M. M. Jones, *J. Am. Chem. Soc.*, **76**, 5995 (1954).

8) R. T. Claunch, T. W. Martine, and N. M. Jones, *J. Am. Chem. Soc.*, **83**, 1073 (1961).

9) H. Horiguchi, "Sekigai Kyukozusetsu Soran," Sankyo Shuppan, Tokyo (1979), Chap. 7.

10) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4533 (1961).

11) R. Lozano, J. Martiney, A. Martiney, and A. D. Lōpey, *Polyhedron*, **2**, 977 (1983).

12) A. W. Coats and J. P. Redfern, *Nature (London)*, **201**, 68 (1964).

13) A. Akhavein and J. E. House, Jr., *J. Inorg. Nucl. Chem.*, **32**, 1479 (1970).

14) K. Miyokawa, M. Takumi, S. Kinoshita, and I. Masuda, *Thermochim. Acta*, **95**, 227 (1985).

15) J. Selbin and T. R. Ortolano, *J. Inorg. Nucl Chem.*, **26**, 37 (1964).

16) H. Langfelderová, V. Karia, M. Lirkešová, and J. Gažo, *J. Therm. Anal.*, **26**, 95 (1983).

17) W. K. Grindstaff and N. Fogel, *J. Chem. Soc., Dalton Trans.*, **1972**, 1476.