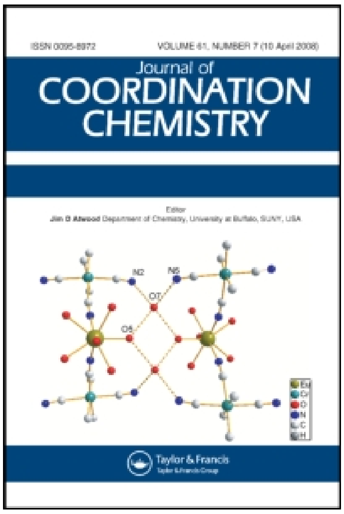


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

KINETICS AND MECHANISM OF ACID DISSOCIATION OF NICKEL(II) COMPLEXES OF NOVEL C-FUNCTIONALIZED MACROCYCLIC DIOXOTETRAAMINES

Huakuan Lin[a]; Shourong Zhu[a]; Appolin Bave Kondiano[a]; Fuping Kou[a]; Yunti Chen[a]
[a] Department of Chemistry, Nankai University, Tianjin, P.R. China

To cite this Article Lin, Huakuan , Zhu, Shourong , Kondiano, Appolin Bave , Kou, Fuping and Chen, Yunti(1999) 'KINETICS AND MECHANISM OF ACID DISSOCIATION OF NICKEL(II) COMPLEXES OF NOVEL C-FUNCTIONALIZED MACROCYCLIC DIOXOTETRAAMINES', Journal of Coordination Chemistry, 46: 3, 291 — 299

To link to this Article: DOI: 10.1080/00958979908048474

URL: http://dx.doi.org/10.1080/00958979908048474

J. Coord. Chem., 1999, Vol. 46, pp. 291–299
Reprints available directly from the publisher
Photocopying permitted by license only

KINETICS AND MECHANISM OF ACID DISSOCIATION OF NICKEL(II) COMPLEXES OF NOVEL C-FUNCTIONALIZED MACROCYCLIC DIOXOTETRAAMINES

HUAKUAN LIN *, SHOURONG ZHU,
APPOLIN BAVE KONDIANO, FUPING KOU and YUNTI CHEN

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

(Received 19 August 1997; In final form 6 January 1998)

The kinetics of the acid dissociation of nickel(II) complexes of a novel C-functionalized macrocyclic dioxotetraamines have been studied using a stopped-flow spectrophotometer. The acid dissociation rate follows the rate law $v_d = C_{com}kK_1K_2[H]^2/(1+K_1[H]+K_1K_2[H]^2)$. Dissociation kinetics are interpreted by a mechanism involving the negatively charged carbonyl oxygen of the complex being rapidly protonated in a pre-equilibrium step, the rate-determining step being intramolecular hydrogen (enolic tautomer) migration (to imine nitrogen). The dissociation rate reaches a plateau in strong acid solution. K_1 and K_2 of the pre-equilibrium step and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the rate-determining step were obtained. Results are compared with those for corresponding copper(II) complexes. The influence of substituents is discussed. Brönsted linear free energy relationships are evident for these C-functionalized complexes.

Keywords: Macrocycles; dioxotetraamines; acid dissociation; kinetics; mechanism; nickel(II)

INTRODUCTION

Acid-assisted dissociation kinetics of open-chain polyamine complexes have been extensively studied[1–10] and reviewed.[9] Recently, there has been considerable interest in the kinetics and mechanism of the acid dissociation of macrocyclic polyamine complexes.[11–14] Most previous work concerns unsubstituted macrocyclic complexes and copper(II). Corresponding kinetics for acid-assisted dissociation of tetraazamacrocyclic nickel(II) complexes with

---

[*] Corresponding author.

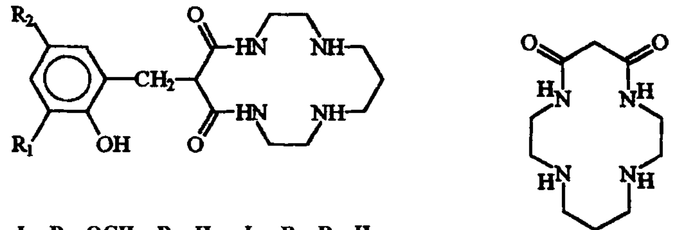
substituents have received little attention. In general, due to thermodynamic and kinetic macrocyclic effects, the complexes are stable and inert, the rates of dissociation of metal complexes with tetraazacycloalkanes being relatively slow. In some instances they are so slow that one can study them only under extreme conditions, such as 10 M $HClO_4$.[11] Dioxotetraamine macrocycles are unique metal chelators; their structures bear the features of macrocyclic polyamines and oligopeptides.[15–20] Macrocyclic dioxotetraamine complexes display interesting properties from the point of view of redox activity and stability. Hay[21] described the kinetics of dissociation of copper(II) and nickel(II) complexes with 1,4,8,11-tetraazacyclotetradecane-12,14-dione (dioxocyclam) in the pH region 4–5, in which the analogous complexes with 14-aneN4 (cyclam) give no sign of dissociation. Because of the carbonyl group, decrease of electron density on the nitrogen atom of the amido group reduced the strength of the C–N bond and caused faster dissociation than for corresponding macrocyclic polyamine complexes. The replacement of the amino group by an amide function can greatly increase the acid dissociation rate of complexes.[21] In a study of complex formation with dioxotetraamine, Kimura[20] considered that the existence of the non-deprotonated or singly deprotonated copper(II) complex was unlikely. That is, the dioxotetraamine dissociates both amide hydrogen when coordinated to a 3d metal ion. In view of pH and spectroscopic titrations Kaden[22] considered that the existence of non-deprotonated and singly deprotonated complex is possible. Recently, Kaden[23] obtained the structure of a copper(II) complex with 1,4,8,11-tetraazacyclotetradecane-12-one (oxocyclam), and indicated that the positions of protonation were the carbonyl oxygen atoms. Structures of macrocyclic dioxotetraamines[18] further indicated that the singly deprotonated complex MLH_{-1} exists in the formation of MLH_{-2}. Non-deprotonated copper(II) complexes of dioxotetraamine macrocycles have been prepared.[16] To sum up, we consider that when the amide macrocyclic ligands coordinate with metal ion, protons of first transfer to the carbonyl oxygen atoms and then leave the complex step by step. Siegfried[22] and Hay[21] gave a different acid dissociation mode, but there is no evidence to support their mechanism. This stimulated us to further investigate acid dissociation kinetics and mechanism.

In a previously paper[24] we reported the kinetics and mechanism of the acid dissociation of a copper(II) complex of 6-(2′-hydroxy-3′,5′-substituted benzyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione. In this paper we report the acid dissociation of the nickel(II) complex of 6-(2′-hydroxy-3′,5′-substituted-benzyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione (14-RTADO) in order to further understand how the metal ion influences the rate of acid dissociation.

EXPERIMENTAL

Reagents

All the reagents used were of reagent grade. KNO_3 and chloroacetic acid were recrystallized before use. Redistilled water was used for all the solutions. The ligands 6-(2′-hydroxy-3′,5′-substituted benzyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione were prepared according to a published method (see Scheme 1).[17]



L_1 $R_1=OCH_3$, $R_2=H$ L_2 $R_1=R_2=H$

L_3 $R_1=H, R_2=Br$ L_4 $R_1=R_2=Br$

L_5

SCHEME 1 Structure of the ligands

Instruments

Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer. Stabilities of macrocyclic dioxotetraamine nickel(II) complexes were determined in the same way as reported previously.[17] The pH values were measured by means of a Beckman Φ71 pH meter. Kinetic measurement used a Union Gekin RA-401 stopped flow spectrophotometer.

Kinetic Measurements

The complex and buffer solutions were prepared and the ionic strength of solutions was maintained to $0.1\,mol\,dm^{-3}$ by using KNO_3. The experimental conditions were such that [complex] $= 1 \times 10^{-3}\,mol\,dm^{-3}$; pH values of solutions were adjusted with $1\,mol\,dm^{-3}$ KOH or HNO_3. Complex solutions were prepared by mixing equimolar quantities of ligand and standard

$Ni(NO_3)_2$, followed by adjustment of pH to 7 with KOH and standing over night, after which the complex is fully formed as $[NiH_{-2}L]$. Dissociation was followed at absorption maxima, *i.e.*, 468 nm (L_1), 460 nm (L_2), 450 nm (L_3), 444 nm (L_4) and 466 nm (L_5). Apparent first-order rate constants were obtained over at least 3 half-lives and represent the average of three runs. Reproducibility of the values of k_{obs} was better than ± 5%.

RESULTS AND DISCUSSION

All the complexes have a d–d absorption band at 440–470 nm, but the free ligands have no absorption in this region. In acid dissociation experiments, the absorption at 440–470 nm disappeared without any interference. Under constant hydrogen ion concentration maintained by means of buffer solutions, a first-order reaction with respect to the concentration of nickel(II) complex was observed; that is, the kinetics of acid dissociation of the nickel(II) complexes follows the rate law

$$v_d = k_{obs} C_{com}, \tag{1}$$

where C_{com} is the total concentration of the complex and k_{obs} is the *pseudo*-first-order rate constant. The relationships k_{obs} values *vs* the hydrogen ion concentration for different temperatures are plotted in Figures 1 and 2.

From the figures, the same phenomena are seen as those reported previously.[24] We see that k_{obs} increases rapidly with increasing of $[H^+]$ at low hydrogen ion concentrations; further increase of $[H^+]$ causes k_{obs} to increase slowly, and then k_{obs} reaches a constant. Our work indicates that the mechanism proposed in a previous paper[24] is correct. Although the crystal structure of the singly deprotonated 14-membered macrocyclic dioxotetraamine nickel(II) complex investigated in this paper was not obtained, we consider that the first and second steps of the acid dissociation (see Scheme 2) involve the protonation of the negatively charged carbonyl oxygen atoms. The rates are very rapid and constitute pre-equilibrium processes. The third step is the migration of protons from the amido oxygen to the amido nitrogen with simultaneous release of nickel(II). This is the rate-determining step. The final step is the very fast protonation of the free ligand.

From the following stoichiometric relation

$$C_{com} = [ML] + [MH_{-1}L] + [MH_{-2}L], \tag{2}$$

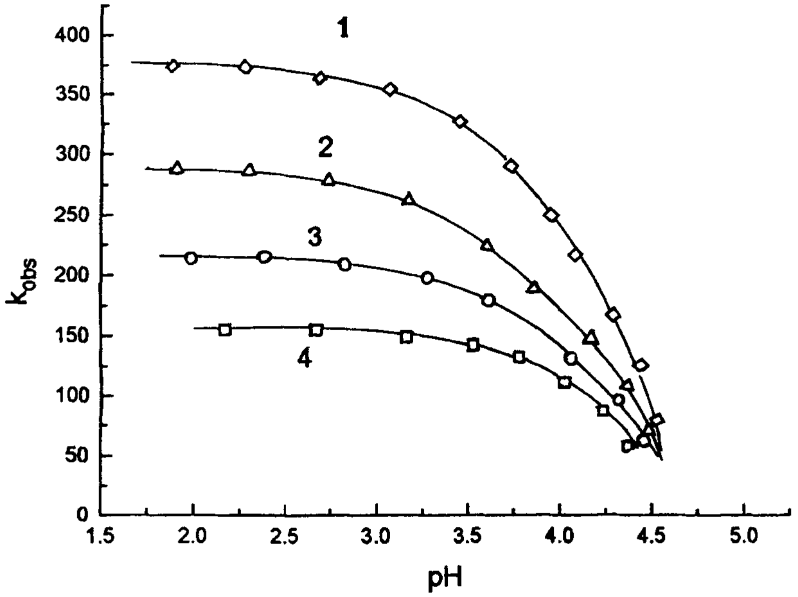


FIGURE 1 A plot of k_{obs} *vs* pH for $CuH_{-2}L_1$; 1: 5°C; 2: 15°C; 3: 25°C; 4: 35°C.

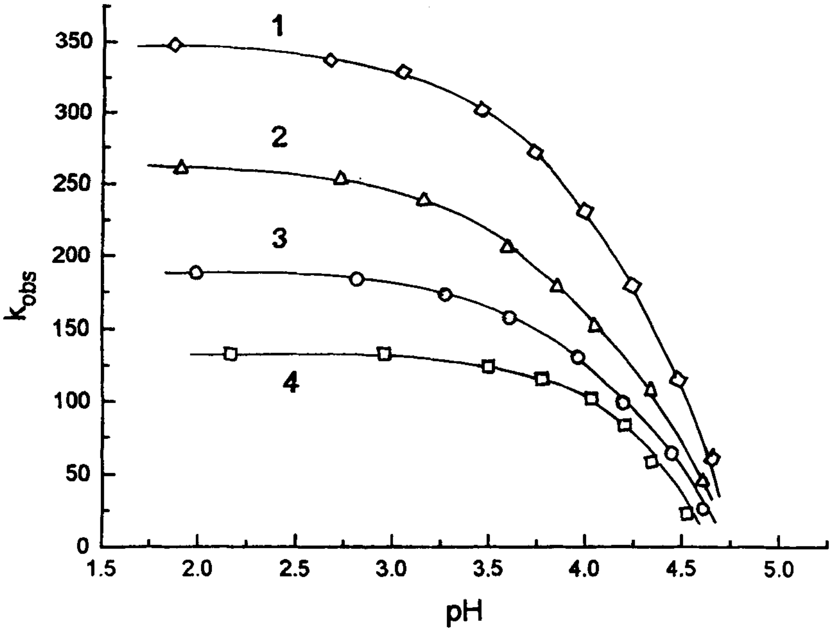
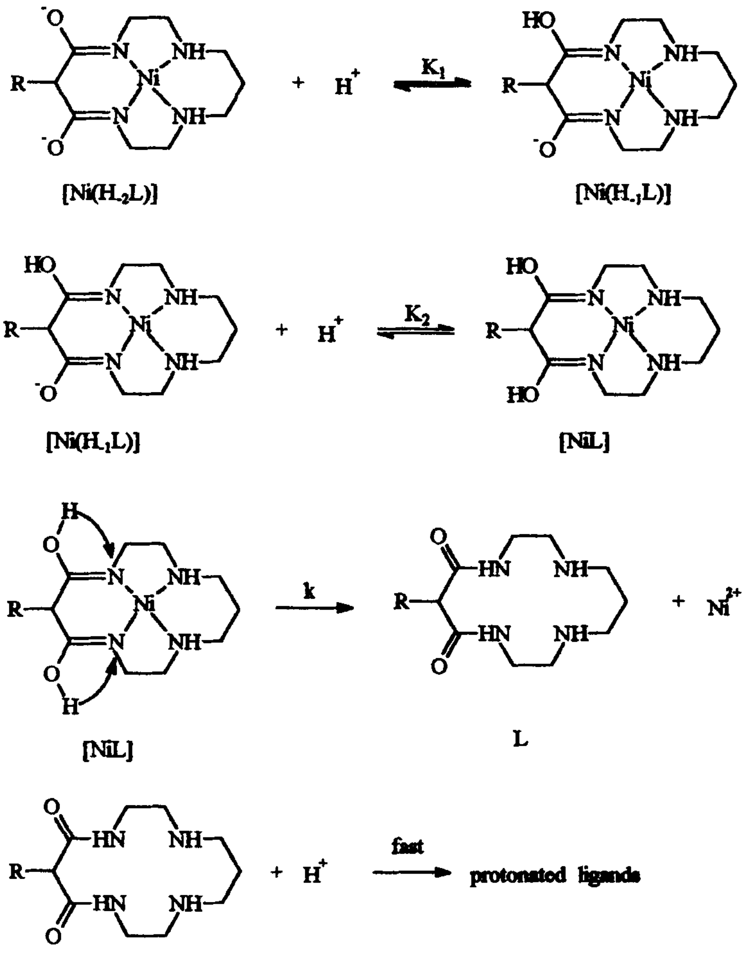


FIGURE 2 A plot of k_{obs} *vs* pH for $CuH_{-2}L_3$; 1: 5°C; 2: 15°C; 3: 25°C; 4: 35°C.



SCHEME 2 Proposed acid dissociation mechanism

we have

$$C_{\mathrm{com}} = [\mathrm{ML}](1 + K_1[\mathrm{H}] + K_1K_2[\mathrm{H}]^2)/K_1K_2[\mathrm{H}]^2 \tag{3}$$

and according to the mechanism, the following:

$$v_{\mathrm{d}} = k[\mathrm{ML}] = C_{\mathrm{com}}K_1K_2[\mathrm{H}]^2/(1 + K_1[\mathrm{H}] + K_1K_2[\mathrm{H}]^2), \tag{4}$$

$$k_{\mathrm{obs}} = kK_1K_2[\mathrm{H}]^2/(1 + K_1[\mathrm{H}] + k_1K_2[\mathrm{H}]^2). \tag{5}$$

From non-linear least-squares fitting of the experimental data using (5), we obtain the values of k, K_1 and K_2 and these are listed in Tables I–III.

TABLE I Rate constant data at various temperatures and thermodynamic properties for the reactions of the complexes at $I = 0.1$ M

Complex	5°C	15°C	25°C	35°C	45°C	$\Delta H^{\neq}_{m}$/kJ mol^{-1}	$\Delta S^{\neq}_{m}$/J K^{-1}mol^{-1}
14-membered Ni(II) complexes							
$\mathrm{CuH_{-2}L_1}$	167.7	226.6	300.3	391.1		17.7	−138.2
$\mathrm{CuH_{-2}L_2}$	156.6	214.9	288.9	381.1		18.7	−135.1
$\mathrm{CuH_{-2}L_3}$	132.4	187.7	259.8	352.5		20.8	−128.8
$\mathrm{CuH_{-2}L_4}$	115.5	169.0	241.0	335.6		22.9	−122.5
$\mathrm{CuH_{-2}L_5}$	137.4	200.0	284.0	394.3		22.6	−112.1
14-membered Cu(II) complexes[24]							
$\mathrm{CuH_{-2}L_1}$		9.45	16.75	29.54	49.15	39.51	−88.9
$\mathrm{CuH_{-2}L_2}$		8.05	13.98	25.06	43.89	40.77	−86.0
$\mathrm{CuH_{-2}L_3}$		6.49	11.74	21.34	37.05	41.86	−83.9
$\mathrm{CuH_{-2}L_4}$		5.08	9.47	17.42	32.37	44.50	−76.9
$\mathrm{CuH_{-2}L_5}$		11.32	19.54	35.24	56.99	38.94	−89.4

TABLE II Data for the pre-equilibrium constant $K_1 \times 10^4$, ΔH_1° and ΔS_1 at $I = 0.1$ mol dm^{-3}

Complex	5°C	15°C	25°C	35°C	ΔH°_{m1}/kJ mol^{-1}	ΔS°_{m1}/J K^{-1}mol^{-1}
$\mathrm{CuH_{-2}L_1}$	4.52	2.70	2.07	0.41	−52.8	−98.8
$\mathrm{CuH_{-2}L_2}$	3.81	2.25	1.55	0.36	−52.8	−100.6
$\mathrm{CuH_{-2}L_3}$	3.82	1.95	1.44	0.35	−52.8	−101.1
$\mathrm{CuH_{-2}L_4}$	2.87	1.83	1.39	0.31	−48.7	−88.1
$\mathrm{CuH_{-2}L_5}$	5.13	4.42	2.54	0.53	−51.9	−93.5

TABLE III Data for the pre-equilibrium constant $K_2 \times 10^4$, ΔH_2° and ΔS_2°, at $I = 0.1$ mol dm^{-3}

Complex	5°C	15°C	25°C	35°C	ΔH°_{m2}/kJ mol^{-1}	ΔS°_{m2}/J K^{-1}mol^{-1}
$\mathrm{CuH_{-2}L_1}$	4.36	2.62	2.02	0.40	−52.3	−97.3
$\mathrm{CuH_{-2}L_2}$	3.82	2.10	1.49	0.35	−53.0	−101.3
$\mathrm{CuH_{-2}L_3}$	3.82	1.95	1.44	0.35	−52.8	−101.1
$\mathrm{CuH_{-2}L_4}$	3.27	1.78	1.35	0.32	−51.1	−96.0
$\mathrm{CuH_{-2}L_5}$	5.13	4.17	3.13	0.47	−52.2	−94.5

From Eyring's equation

$$\mathrm{Ln}(k/T) = -\Delta H^{\neq}_{m}/RT + \Delta S^{\neq}_{m}/R + \ln(R/N_a h), \qquad (6)$$

activation parameters $\Delta H^{\neq}_{m}$ and $\Delta S^{\neq}_{m}$ of the rate-controlling step can be obtained. K_1 and K_2 values are the equilibrium constants for the first and second pre-equilibrium steps, respectively:

$$MH_{-2}L + H = MH_{-1}L, \tag{7}$$

$$MH_{-1}L + H = ML. \tag{8}$$

Using Eq. (9),

$$\mathrm{Ln}\, K = -\Delta H^{\circ}_{\mathrm{m}}/RT + \Delta S^{\circ}_{\mathrm{m}}/R, \tag{9}$$

thermodynamic parameters for pre-equilibrium steps can be obtained. Activation parameters $\Delta H^{\neq}_{\mathrm{m}}$ and $\Delta S^{\neq}_{\mathrm{m}}$ are also listed in Table I with the rate-constant k; the thermodynamic parameters $\Delta H^{\circ}_{\mathrm{m}}$, $\Delta S^{\circ}_{\mathrm{m}}$ are listed in Tables II and III with corresponding equilibrium constants. For the sake of comparison, the rate constant, k, and $\Delta H^{\neq}$, $\Delta S^{\neq}$ of corresponding 14-membered copper(II) systems are also listed in Table I.

From Table I it is seen that values of k decrease with change of complex from $NiH_{-2}L_1$ to $NiH_{-2}L_4$ (substituents change from CH_3O to 2Br). Values decrease with a decrease of the base strength of the macrocyclic dioxotetraamine ligand. The stronger the base strength of the macrocyclic dioxotetraamine ligands, the faster the intramolecular hydrogen migration. Linear regression of the rate constants as $\log k$ to the protonation constants $\log \beta_1$ ($L_1(CH_3O)$ 10.21; L_2(H) 10.08; L_3(Br) 9.82; L_4(2Br) 9.55[25]) gave the following equation (25°C):

$$\log k = 4.962 + 0.1484 \log \beta_1; \quad r = 0.997. \tag{10}$$

This indicates that Brönsted linear free energy relationships do exist for these C-functionalized dioxotetraamine nickel(II) complexes. From Table I it is also seen that the values of k for 14-membered nickel(II) systems are larger than for 14-membered copper(II) systems. The formation of nickel(II)-14-RTADO complexes is more difficult than copper(II)-14-RTADO complexes. In pH titrations values are not stable after addition of KOH solution to nickel(II)-14-RTADO for 2–3 h, but are stable in the copper (II)-14-RTADO binary system after 2–3 min. Furthermore, the stabilities of Cu(II)-14-RTADO complexes are greater than nickel(II)-14-RTADO complexes. Therefore, the rate constants for acid-dissociation of nickel(II)-14-RTADO complexes are larger. From Tables II and III it is seen that ΔH°_1, ΔH°_2, ΔS°_1 and ΔS°_2 are negative. This can be understood in terms of a simple neutralization reaction.

From the above results, we also understand that the acid dissociation rate constants for unsaturated complexes of macrocyclic dioxotetraamines are larger than for corresponding analogous saturated complexes. Because the carbonyl group largely decreases the electron density on the nitrogen atom of amide, this reduces the stabilities of complexes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Project 29671020).

References

[1] D.W. Margerum, D.B. Rorabacher and F.G. Clarke, *Inorg. Chem.*, **2**, 667 (1963).
[2] A.K.S. Ahmed and R.G. Wilkins, *J. Chem. Soc.*, 2901 (1960).
[3] G.A. Melson and R.G. Wilkins, *J. Chem. Soc.*, 2662 (1962); *ibid.*, 4475 (1962).
[4] A.K.S. Ahmed and R.G. Wilkins, *Proc. Chem. Soc.*, 399 (1959).
[5] A.K.S. Ahmed and R.G. Wilkins, *J. Chem. Soc.*, 3700 (1959); *ibid.*, 2895 (1960).
[6] R.F. Childers and R.A.D. Wentworth, *Inorg. Chem.*, **8**, 2218 (1969).
[7] D.C. Weatherburn, E.J. Billo, J.P. Jones and D.W. Margerum, *Inorg. Chem.*, **9**, 1557 (1970).
[8] G.B. Kolski and D.W. Margerum, *Inorg. Chem.*, **8**, 1129 (1969).
[9] D.W. Margerum, G.R. Cayley, D.C. Weatherburn and G.K. Pagenkopf, *ACS Monogr.*, **174**, 1 (1978).
[10] R.A. Read and D.W. Margerum, *Inorg. Chem.*, **20**, 3143 (1981).
[11] A.K. Pondit, A.K. Das and D. Barerjia, *Trans. Met. Chem.*, 437 (1988).
[12] C.C. Chang and C.S. Chung, *J. Chem. Soc., Dalton Trans.*, 1965 (1991).
[13] B.F. Liang and C.S. Chung, *Inorg. Chem.*, **22**, 1017 (1983); *ibid.*, **20**, 2152 (1981).
[14] L.H. Chen and C.S. Chung, *Inorg. Chem.*, **27**, 1980 (1988); *ibid.*, **25**, 2841 (1986).
[15] Q.H. Luo, S.R. Zhu, M.C. Shen, A.B. Dai, A.D. Liu, H.C. Gu, F.M. Li and S.J. Di, *Kexue Tongbao*, 1288 (1992); M.C. Shen, Q.H. Luo, S.R. Zhu, Q.Y. Tu, A.B. Dai, A.D. Liu, H.C. Gu, F.M. Li and S.J. Di, *Chem. J. Chinese Univ., Series B*, **6**, 354 (1990).
[16] Q.H. Luo, R.S. Zhu, M.C. Shen, S.Y. Yu, Z. Zhang, X.Y. Huang and Q.J. Wu, *J. Chem. Soc., Dalton Trans.*, 1873 (1994).
[17] S.R. Zhu, H.K. Lin, C.C. Lin, F.P. Kou and Y.T. Chen, *Inorg. Chim. Acta*, **228**, 225 (1995).
[18] F.P. Kou, S.R. Zhu, H.K. Lin, Y.T. Chen, H.G. Wang and X.K. Yao, *J. Chem. Soc., Chem. Commun.*, 59 (1996).
[19] H.K. Lin, S.R. Zhu, Z.X. Gu and Y.T. Chen, *J. Chem. Soc., Dalton Trans.*, 1879 (1995).
[20] E. Kimura, *J. Coord. Chem.*, **15**, 1 (1986).
[21] R.W. Hay, M.P. Pujari and F. McLaren, *Inorg. Chem.*, **23**, 3033 (1984).
[22] L.C. Siegfried and T.A. Kaden, *J. Phys. Org. Chem.*, **5**, 549 (1992).
[23] L.C. Siegfried, M. Neuburger, M. Zehnder and T.A. Kaden, *J. Chem. Soc., Chem. Commun.*, 951 (1994).
[24] Fuping Kou, Shouring Zhu, Huakuan Lin, Wangdong Chen, Yunti Chen and Meirong Lin, *Polyhedron*, **16**, 2021 (1997).
[25] Lin Huakuan, Zhu Shourong, Appolin B. Kondiano, Kou Fuping and Chen Yunti, *Acta Physico-Chimica Sinica*, **13**, 417 (1997).