Polish J. Chem., **77**, 917–921 (2003) **COMMUNICATION**

Synthesis, Characterization and Activity of Rare Earth Complexes with Schiff Base from Picolinaldehyde N-Oxide and 4,4′-Methylenedianiline

by Q. Yu[1], K. Chen[2] and M.Y. Tan[1*]

[1]*College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China*
[2]*College of Life Science, Lanzhou University, Gansu 730000, P. R. China*

(Received July 8th, 2002; revised manuscript January 17th, 2003)

Many transition metal complexes of Schiff base containing pyridine N-oxide and its substituted derivatives have been reported [1–3]. Rare earth ions are known to form complexes with many Schiff bases [4]. But to our knowledge, complexes of rare earth ions with Schiff base containing 2-pyridinecarboxaldehyde N-oxide have never been reported before. In the study of the coordination behavior of rare earth ions with Schiff base from picolinaldehyde N-oxide, in this paper, six new complexes of the formula $[RE_2L_3(NO_3)_4\cdot 2H_2O](NO_3)_2\cdot nH_2O$ (RE = La, Pr, n = 4; RE = Eu, Tb, Er, Y, n = 5; L = bis(N-(2-iminopyridine N-oxide)-4,4′-diamino-diphenyl)methane (Fig. 1)) were synthesized, and their biological activities were investigated. It was found that the complexes had similar activity on wheat growth regulation. They all have good activity at low concentration, while exhibit inhibition at high concentration.

All reagents used in this work were of analytical grade without further purification. Picolinaldehyde N-oxide was synthesized using published procedures [5]. RE(III) nitrate solutions were prepared from the reaction of RE(III) oxide with nitric

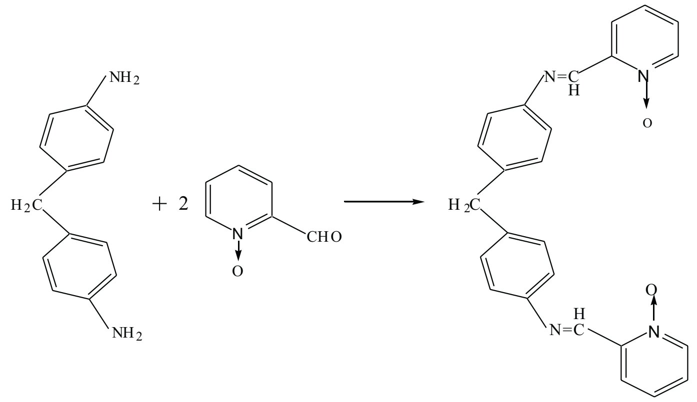

Figure 1. Formation of ligand bis(N-(2-iminopyridine N-oxide)-4,4′-diamino-diphenyl)methane.

---

[*] Address for correspondence to Min Yu Tan (E-mail: tangyu@lzu.edu.cn)

acid. The ligand (L) was prepared by mixing a solution (30 mL) of picolinaldehyde N-oxide (5.2 g, 42 mmol) with 4,4′-methylenedianiline (4.0 g, 20 mmol) in ethanol (30 mL). The resulting solution was refluxed for 4 h. On cooling, a yellow precipitate was separated, which was filtered, washed with anhydrous ethanol, and dried *in vacuo.* The yield of L was 6.5 g (80%) and m.p. 117–118°. L was insoluble in C_2H_5OH, CH_3CN, partially soluble in CH_3OH, H_2O, however, freely soluble in $CHCl_3$, DMF, and DMSO. ^1H NMR (DMSO-d_6) δ: 4.95 (m, 2H, >CH_2), 6.30–6.90 (m, 8H, Py), 7.22–7.54 (m, 8H, Ph), 9.06 (s, 2H, -CH=N). The complexes were prepared as follows: A $C_2H_5OH/CHCl_3$ (10 mL) solution (V/V = 3/2) of RE(III) nitrate (3 mmol) was added drop-wise to solution (10 mL) of the L (2 mmol) and stirred for 6 h to give a light yellow precipitate. The precipitate was collected, washed with ethanol and dried *in vacuo.* The yields of the complexes are shown in Table 1. The biological activity was investigated as follows: Seeds of the spring wheat (Triticum aestivum L. CV. LongChun 18) which were rinsed with tap water germinated at dark for 24 h and grew in Hoagland cultures at 20 ± 1°C in 12 h light (60 μmol· m^{-2} · s^{-1})/12 h dark cycle. The additions of complexes were 5, 10, 20, 30 μmol/L.

(1) Germination Rate: 5 days later, collecting 100 seeds in randomization germination rate was calculated. The germination rate is a ratio of germinated seeds to all. (2) Root Length Measurement: After germinating 7 days, 20 roots were collected and the lengths were measured. The mean value was obtained. (3) Total Chlorophyll Content: After 10 days, 0.5 g leaves was collected. Chlorophyll a and b were extracted with 80% acetone, and then quantified spectrophotometrically [6]. (4) Nitric Reductase (NR) Activity Estimation: After treatment 12 days, addition of 50 mmol/L KNO_3 induced formation of NR before estimating NR activity. After 3 g leaves were homogenized in freezing condition, the fractions were prepared according to the method [7], and buffer (25 mmol PBS + 1 mmol EDTA + 10 mmol Cys, pH = 8.8) was added. After centrifuged at 10000 g for 20 min, the supernate was used as enzyme crude extract. 0.2 mL enzyme crude extract, 0.5 mmol KNO_3 and 0.3 mL NADH (10 mmol) were kept in 25℃ for 30 min, then 10% aminosulfabenzamide and 0.5 mL 1-naphthyl-2,2′-diaminoethene were added into the mixed solution. O. D_{540} was determined after 15 min (0.3 mL H_2O, no NADH as control).

Elemental analyses were carried out with a model GM Elementar Vario EL. The molar conductivity was measured with a DDSJ-308 conductivity meter. Infrared spectra of L and its complexes were recorded as KBr pellets using a FT-IR Nicolet NEXUS 670 spectrophotometer. ^1H NMR spectra were recorded on an Avance DRX-200 NMR spectrometer in DMSO-d_6 solution, using TMS as internal reference. The thermogravimetric measurements in stable air were carried out with a PCD-2 thermal balance at a heating rate of 10°C/min. The elemental analyses indicate that the complexes have a 2:3 (M:L) stoichiometry. The molar conductivity data are shown in Table 1 and the values are in the range expected for 1: 2 electrolytes [8]. The data of infrared spectra of ligand and its complexes are shown in Table 2. The analyses of the thermal curves of the complexes clearly show that two water molecules present in all complexes are lost at ~150°C, the four or five water molecules are lost

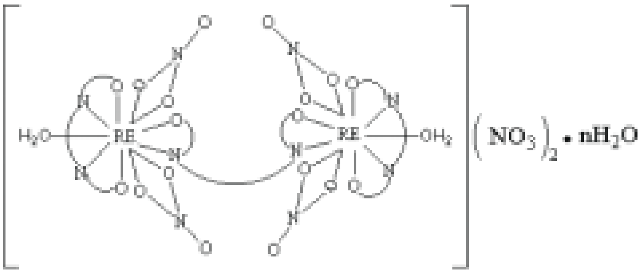

Figure 2. Suggested structure of the complexes.

below 100℃, indicating that two water molecules are coordinated to the RE(III) ion. The complexes do not exhibit a melting point. Between 212–590°C the molecules of the ligand are lost by three continuous exothermic processes. In all cases the final products are the metal oxides. The results show that the complexes have the general structure formula $[RE_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot nH_2O$ (RE = La, Pr, n = 4; RE = Eu, Tb, Er, Y, n = 5). All complexes are stable in air and insoluble in ethanol, chloroform, acetone, acetonitrile and benzene, however, soluble in methanol, DMF and DMSO.

On the basis of the above studies the structure in Figure 2 may be suggested for the complexes.

Table 1. Yield and data of molar conductivity for studied compounds.

No.	Compound/Empirical Formula	Yield (%)	Λ_m^* ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$)
	$L \cdot 1.5H_2O$ $C_{25}H_{23}N_4O_{3.5}$	80	
(1)	$[La_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 4H_2O$ $C_{75}H_{72}N_{18}O_{30}La_2$	60	224.7
(2)	$[Pr_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 4H_2O$ $C_{75}H_{72}N_{18}O_{30}Pr_2$	52	211.7
(3)	$[Eu_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 5H_2O$ $C_{75}H_{74}N_{18}O_{31}Eu_2$	47	210.7
(4)	$[Tb_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 5H_2O$ $C_{75}H_{74}N_{18}O_{31}Tb_2$	50	188.7
(5)	$[Er_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 5H_2O$ $C_{75}H_{74}N_{18}O_{31}Er_2$	47	182.7
(6)	$[Y_2L_3(NO_3)_4 \cdot 2H_2O](NO_3)_2 \cdot 5H_2O$ $C_{75}H_{74}N_{18}O_{31}Y_2$	45	207.7

*25°C, 10^{-3} $mol \cdot L^{-1}$ in methanol.

Table 2. Data of IR, ^{1}H NMR and TG-DTA for compounds.

Compd.	IR, ν (cm^{-1})						^{1}H NMR (DMSO-d_6) δ -CH=N-	TG-DTA (℃, %)	
	N→O	>CH=N-	NO_3^-					DTA* peak (°C)	Weight loss (%)**
			D_{3h}	ν_1	ν_3	ν_4			
L	1236, 853	1426					9.0 (s, 2H)		
(1)	1216, 855	1437	1384	1482	817	1301	9.0 (m, 6H)	100; 157	3.8 (3.6); 2.2 (1.8)
(3)	1213, 857	1437	1383	1487	815	1295		54; 148	4.9 (4.4); 1.6 (1.8)
(5)	1212, 856	1437	1383	1506	814	1299		88; 150	4.9 (4.4); 1.2 (1.8)

*Endothermic process
**Calculated values in parentheses

It is found from the biological activity tests that the compounds have similar activity on wheat regulation. Complexes **(1)–(6)** inhibit germination and promote rooting. Chlorophyll content is a symbol for photosynthesis. Chlorophyll content decreases along with the complexes content increase. NR activity is a symbol for nitrogen utilization ratio and represents nitrogen nourishment level. All the complexes have good activity at low concentration (5–10μmol/L), while inhibition at high concentration.

The results of biological activity test are recorded in Figs. 3–6.

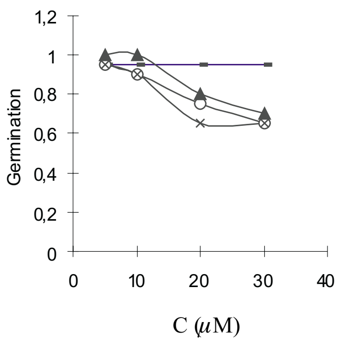

Figure 3. Influence to germination.

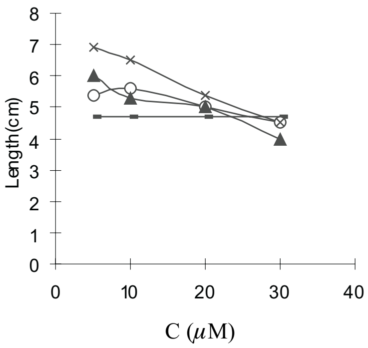

Figure 4. Influence to root length.

– Control; o Ligand; ▲ Complex (**3**); x Europium Nitrate

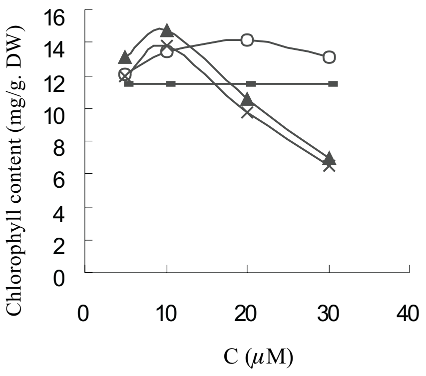

Figure 5. Influence to chlorophyll content.

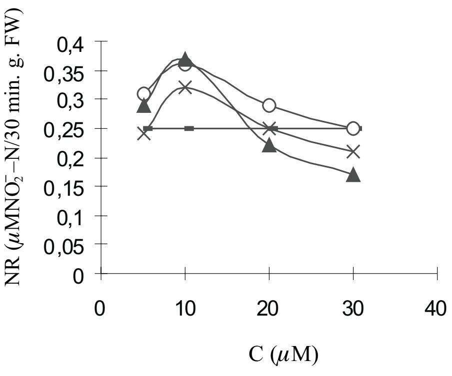

Figure 6. Influence to nitric reductase.

– Control; o Ligand; ▲Complex (**3**); x Europium Nitrate

REFERENCES

1. Boca M., Baran P., Boca R., Fuess H., Kickelbick G., Linert W., Renz F. and Svoboda I., *Inorg. Chem.*, **39**, 3205 (2000).
2. Gembicky M., Baran P., Boca R., Fuess H., Svoboda I. and Valko M., *Inorg. Chim. Acta*, **303**, 75 (2000).
3. Gou Shaohua, You Xiaozeng, Yu Kaibei and Lu Jianping, *Inorg. Chem.*, **32**, 1883 (1993).
4. Siddiqi K.S., Basher A., Tabassum S. and Zaidi S.A.A., *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 217 (1991).
5. Jerchel D. and Heider J., *Liebigs Ann. Chem.*, **613**, 153 (1958).
6. Lichtenthaler H.K., *Methods Enzymol*, **148**, 350 (1987).
7. Matsubaba T. and Iwasaki H., *J. Biochem.*, **69**, 859 (1971).
8. Gearry W.J., *Coord. Rev.*, **7**, 81 (1971).