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Thermo-decomposition kinetics and representative structure of homologous dinuclear complexes

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Abstract

The title complex with formally heptadentate dinucleating ligands L, $[Ni_2L_2](py)_2(H_2O)_2$ (L = $C_{31}H_{28}N_2O_7$ dianion), was synthesized, characterized by elemental analyses and IR spectroscopy, and structurally determined by X-ray diffraction technique. In the center-symmetric unit $[Ni_2L_2]$, two phenolates and two Schiff-base imino groups of each L, as a practical tetradentate ligand, bond two Ni atoms to form square-distortionally tetrahedral coordination geometries, D_{2d} symmetry. This nickel(II) complex and its homologue $[Cu_2L_2](py)_2(H_2O)_2$ were both studied by TG–DTG technique under non-isothermal conditions. The relationship between weight loss and coordinations of L in each complex was inferred in the thermal decomposition processes. The most probable kinetic mechanism, Zhuralev–Lesokin–Tempelman equition, was determined by using the combined differential and integral methods, and the related values of activation energy E and pre-exponential factor A were calculated, respectively, for each complex. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dinuclear complex; Kinetics; Nickel(II); Structure; Thermal decomposition

1. Introduction

Interest in the study of the transition metal (M) dinuclear complexes is increasing [1,2]. Besides designing, synthesizing and determination of the structure of the compounds as models of poly-metal enzymes (proteins), the research on their properties always involves electro- and/or magneto-chemistry, where the interactions between M···M centers in the same molecule can be shown. But to this end, few studies on thermochemistry, so far as we know, have been reported.

As part of our continuous work, the homologue $[Cu_2L_2](py)_2(H_2O)_2$ has been structurally determined and cyclo-voltammetrically measured. The results indicate that its structure is very similar to that of the title Ni(II) complex, and the Cu···Cu interaction exists in the electrolyte solution of this Cu(II) complex [3]. In this paper, we try to find out the thermochemical manifestation of the M···M interaction in every homologous dinuclear complex molecule.

Corresponding to Fig. 1, the structural formula of $[Ni_2L_2]$ unit with the heteroatom numbers is drawn below, where the dotted lines are the cracking positions on the thermal decomposition step II for both homologues.

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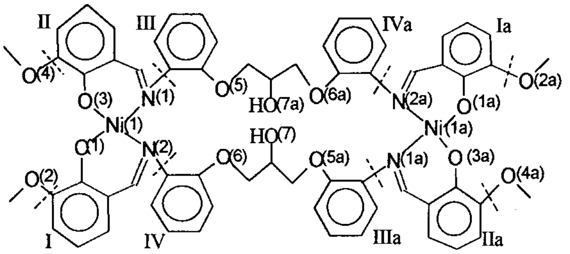


2. Experimental

2.1. Synthesis of $[Ni_2L_2](py)_2(H_2O)_2$

2.1.1. Materials and measurements

All starting materials were commercial products of chemical or analytic grade purity and were used without further purification. Elemental analyses and IR spectra were carried out on a Perkin-Elemer 240 C microanalyser and a Nicolet 5DX FT spectrophotometer as KBr disks in the range 4000–400 cm^{-1}, respectively.

The ligand $H_2L{\cdot}0.5H_2O$, 1,3-di[*o*-(*o*-vanillideneimino)phenoxo]-2-propanol semi-hydrate, and its single-crystal copper(II) complex $[Cu_2L_2](py)_2(H_2O)_2$ were prepared according to the literature methods [3].

2.1.2. Synthesis and single crystal growth

$H_2L{\cdot}0.5H_2O$ (0.55 g, 1 mmol) was added slowly in portions to a stirred solution of $Ni(OAc)_2{\cdot}4H_2O$ (0.25 g, 1 mmol) in MeOH (30 cm^3) at room temperature. After the mixture was refluxed for 4 h, the resultant yellow-green powder was filtered off, washed with cold MeOH and dried in air. Then it was re-dissolved in appropriate amount of pyridine. The red crystals $[Ni_2L_2](py)_2(H_2O)_2$, suitable for X-ray structure determination and used as the sample of the TG–DTG experimental, were separated off by natural evaporation of the solvent during 10 days. Found: C, 61.3; H, 5.3; N, 6.0. Calculated for $C_{72}H_{70}N_6O_{16}Ni_2$: C, 62.0; H, 5.0; N, 6.0. IR (cm^{-1}): 3378 [s, br, ν(OH)]; 1640, 1615 [vs, sh, ν(C=N)]; 1257 [s, sh, ν(Ar–O–R)].

2.1.3. Suggestion of the IR spectrum

In form, the IR spectrum of the Ni(II) complex is very similar to that of the copper(II) complex. As an evidence for the coordination of imino group, the absorption band of C=N stretching mode has been

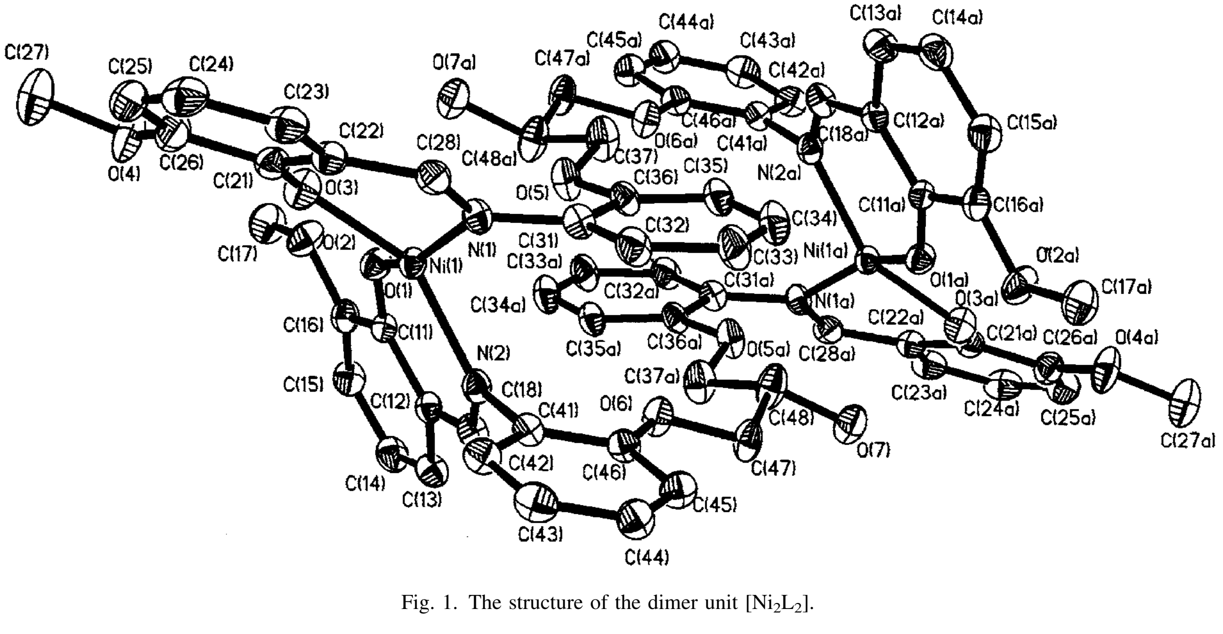


Fig. 1. The structure of the dimer unit $[Ni_2L_2]$.

splited from the single peak at 1620 cm^{-1} in the spectrum of the free ligand [3].

2.2. *X-ray structure determination of $[Ni_2L_2](py)_2(H_2O)_2$*

2.2.1. *Crystal data*

$C_{72}H_{70}N_6O_{16}Ni_2$: $M_r = 1392.81$, triclinic, space group $P-1$ (No. 2), $a = 10.206(2)$ Å, $b = 12.097$ Å, $c = 14.500(4)$ Å, $\alpha = 104.76(3)^\circ$, $\beta = 90.83(2)^\circ$, $\gamma = 110.69(2)^\circ$, $V = 1608(1)$ Å^3, $Z = 1$, $D_x = 1.438$ g cm^{-3}, $F(0\,0\,0) = 728$, $\mu = 0.660\ \text{mm}^{-1}$.

2.2.2. *Data collection and refinement of crystal structure*

A crystal with approximate dimension of 0.25 mm ×0.3 mm × 0.3 mm was mounted on a glass fiber in an arbitrary orientation. The determination of unit cell and the data collection were performed on an Enraf-Nonius CAD4 four-circle diffractometer at 293(2) K with a graphite monochrometer situated in the incident beam with Mo Kα radiation ($\lambda = 0.71073$ Å) using an $\omega - 2\theta$ scan mode. A total of 4120 independent reflections were collected in the range of $2^\circ \leq \theta \leq 23^\circ$, of which 3117 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. The correction for *LP* factors were applied to the data.

The structure was solved by direct method (Multan 82). The location of Ni atom was determined from an *E*-map. The other non-hydrogen atoms were determined with successive differential Fourier syntheses. Hydrogen atoms were introduced in calculated positions, but not refined. The final refinement by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms was converged with non-weighted and weighted agreement factors of $R = 0.067$ and $R_w = 0.069$ ($w = 1/\sigma^2(F_0) + 99.0000F^2$), $(\Delta/\sigma)_{\max} = 2.42$, $S = 1.74$. The maximum and minimum residuals had heights of 0.45 and −0.37 eÅ^{-3}.

2.3. *TG–DTG measurements of $[M_2L_2](py)_2(H_2O)_2$ (M = Ni or Cu)*

The experiments were carried out on a Perkin-Elemer TGA7 thermogravimetric analyzer in N_2 atmosphere (60 $\text{cm}^3\ \text{min}^{-1}$), at the heating rate of

Table 1
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients[a] (Å^2 ×10^3)

Atoms	x	y	z	U(eq)
Ni(1)	459(1)	3139(1)	2077(1)	36(1)
O(1)	−856(4)	1893(4)	1044(3)	45(1)
O(2)	−2953(4)	71(4)	−35(3)	59(1)
O(3)	−567(5)	2268(4)	2938(3)	55(1)
O(4)	−1718(5)	559(4)	3752(4)	80(1)
O(5)	−235(4)	4888(4)	1712(3)	53(1)
O(6)	3003(4)	5398(4)	482(3)	50(1)
O(7)	2877(5)	6988(4)	−1274(3)	62(1)
N(1)	1238(5)	4684(4)	3119(3)	41(1)
N(2)	2025(5)	3481(4)	1243(4)	41(1)
C(11)	−614(5)	1427(5)	186(4)	39(1)
C(12)	668(6)	1841(5)	−188(4)	39(1)
C(13)	864(6)	1271(5)	−1120(4)	49(1)
C(14)	−217(6)	286(5)	−1682(5)	56(1)
C(15)	−1517(6)	−151(5)	−1337(4)	53(1)
C(16)	−1716(6)	409(5)	−434(4)	45(1)
C(17)	−4128(7)	−941(6)	−604(5)	71(1)
C(18)	1891(6)	2849(5)	360(4)	46(1)
C(21)	−177(6)	2557(5)	3841(4)	46(1)
C(22)	760(6)	3713(5)	4412(4)	44(1)
C(23)	1103(6)	3925(6)	5398(4)	57(1)
C(24)	516(7)	2996(6)	5825(5)	65(1)
C(25)	−432(7)	1846(6)	5296(5)	61(1)
C(26)	−769(6)	1642(6)	4344(5)	58(1)
C(27)	−2498(8)	−364(7)	4187(6)	99(1)
C(28)	1292(6)	4729(5)	4009(4)	46(1)
C(31)	1725(6)	5811(5)	2868(4)	43(1)
C(32)	2928(6)	6788(5)	3320(5)	54(1)
C(33)	3331(6)	7883(5)	3066(5)	60(1)
C(34)	2503(7)	7971(5)	2331(5)	62(1)
C(35)	1280(6)	7003(5)	1881(5)	53(1)
C(36)	918(6)	5932(5)	2127(4)	42(1)
C(37)	−1288(6)	4982(6)	1116(5)	63(1)
C(41)	3368(5)	4412(5)	1598(4)	39(1)
C(42)	4156(6)	4340(5)	2345(4)	48(1)
C(43)	5474(6)	5257(6)	2697(5)	58(1)
C(44)	5984(6)	6238(5)	2307(5)	55(1)
C(45)	5187(6)	6314(5)	1557(5)	50(1)
C(46)	3875(5)	5401(5)	1203(4)	43(1)
C(47)	3526(6)	6298(5)	−23(4)	53(1)
C(48)	2293(6)	6281(6)	−638(5)	62(1)
N(50)	5689(7)	3541(6)	4308(5)	93(1)
C(51)	5918(7)	2571(7)	3732(6)	88(1)
C(52)	4887(7)	1422(6)	3411(5)	84(1)
C(53)	3553(7)	1243(6)	3685(5)	75(1)
C(54)	3310(7)	2203(6)	4260(5)	73(1)
C(55)	4380(7)	3308(6)	4552(5)	80(1)
O(11)	6686(5)	−20(5)	1924(4)	91(1)

[a] $U(\text{eq}) = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* \cdot a_j^* \cdot a_i \cdot a_j$.

10° min^{-1} and until 900°C. The sample weights of the Ni and Cu complex were 2.474 and 2.632 mg, respectively.

When the heating was performed at a rate of 5° min^{-1}, TG–DTA measurements of the two complexes were recorded on a LCT-2 thermo-balance without data-storage function. Although the results have not been reported here, no practical characteristic has been observed about the two TG curves resulting from the TG–DTA spectra which differ from those obtained from the TG–DTG in this paper.

3. Results and discussion

3.1. Structure of $[Ni_2L_2](py)_2(H_2O)_2$

The fractional coordinates and the displacement coefficients for non-hydrogen atoms are given in Table 1.

The center-symmetric molecule consists of one dimer coordination unit $[Ni_2L_2]$, as well as two pyridine and two water as crystalline solvent molecules whose nitrogen and oxygen atoms are labeled by N(50) [N(50a)] and O(11) [O(11a)], respectively. In the discrete dimer (see Fig. 1) the phenolate atom O(1) and imino atom N(2), belong to the same deprotoned ligand L, as well as O(3) and N(l), coming from another L, commonly bond Ni(1) atom to form a coordination geometry at Ni(1), being D_{2d} symmetric. The deviations from the calculated coordination plane to every donor and Ni(1) atom are so short (see Table 2) that the geometry at Ni(1) is best described as *cis*-square planar with a slight tetrahedral distortion. Being center-symmetric, every pair of the corresponding phenyl ring planes, I and Ia, etc. see the structural formula, are parallel each other. So also are both coordination planes on Ni(1) and Ni(1a), and there is the separation of 6.80 Å between them. The distance between Ni(1) ··· Ni(1a) is 9.87 Å, but the shortest one between the Ni atoms in the lattice that belong to two units, respectively, is 8.16 Å.

Twisting occurs between the L chains along the direction of their length. Thus, no three oxygen atoms bonding directly to the flexible alkyl group at the middle of one L, O(5a), O(6) and O(7) [or O(5), O(6a) and O(7a)], are involved in the coordination. And the dihedral angle between the phenyl ring planes II and III (IIa and IIIa) or I and IV (Ia and IVa) is 31.8° or 113.2°, although in the free ligand the two rings and the –C=N– group bridged between them co-form a conjugated system, being co-planar.

Table 2
Coordinate bond lengths (Å), angles (°) and deviations (Å) from least-square plane[a] for $[Ni_2L_2](py)_2(H_2O)_2$

Bond lengths	
Ni(1)–N(1)	1.971(4)
Ni(1)–N(2)	2.008(5)
Ni(1)–O(1)	1.918(3)
Ni(1)–O(3)	1.922(5)
Bond angles	
N(1)–Ni(1)–N(2)	98.1(2)
N(1)–Ni(1)–O(1)	157.7(2)
N(1)–Ni(1)–O(3)	91.7(2)
N(2)–Ni(1)–O(1)	93.0(2)
N(2)–Ni(1)–O(3)	151.0(2)
O(1)–Ni(1)–O(3)	87.7(2)
Deviations	
N(1)	0.4063
N(3)	−0.3913
O(1)	0.4393
O(2)	−0.4516
Ni(1)[b]	0.0626

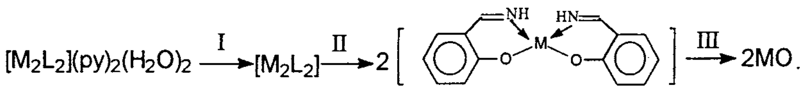
[a] Orthogonal equation is $-0.7801x_0 + 0.5798y_0 - 0.2353z_0 = .1.5466$.

[b] Atom not used to calculate the plane.

The structure is very similar to that of $[Cu_2L_2](py)_2(H_2O)_2$ [3], including the coordination configuration and bond parameters, crystallographic symmetry and even cell parameters, etc.

3.2. Thermal decompositions of $[M_2L_2](py)_2(H_2O)_2$ (M = Ni or Cu)

The TG–DTG curves of two complexes are shown in Figs. 2 and 3, respectively; the data on weight losses are listed in Table 3; their successive three steps may be expressed as shown:



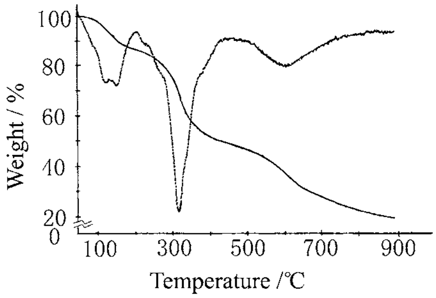


Fig. 2. TG–DTG curves of $[Ni_2L_2](py)_2(H_2O)_2$: (—) TG, (– ·· –) DTG.

Due to limitations in the analyzer used, the decomposition of the Ni complex was not complete until 900°C. In step I for Cu complex, the value of the weight loss found was less than that of the calculated value, which may be due to surface efflorescence of the sample.

From the view of coordination chemistry, each of the similar decomposition steps of two complexes has the same origin. In the first step the weight losses involve both the crystalline solvent molecules of pyridine and water, since they exist in the outer-spheres of the complexes. With heating, two well-separated peaks are displayd on the DTG curve of every complex. This indicates that the decomposition of the ligand divides into two steps, II and III. Correspondingly, only an incline with less slope (no clear plateau) appears on the TG curve between II and III. It is conjectured, based on both the percentages of weight losses and complexation sustainment, that in step II, one Schiff-base ligand L loses its greater part (see the structural formula), and the remaining fragments, two isolated salicylidenimino groups, persist in their coordination to two metal ions, respectively, with stable six-member conjugate chelate rings.

Unfortunately, as one original dinuclear unit has been transformed into two mononuclear units, the expected M···M interaction, existing only in the same unit, cannot occur between the units. Of course, another possibility should be considered that this interaction originally do not exist within any dinuclear unit of the crystal states.

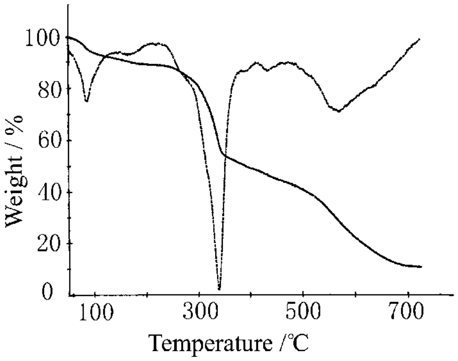


Fig. 3. TG–DTG curves of $[Cu_2L_2](py)_2(H_2O)_2$: (—) TG, (– ·· –) DTG.

3.3. Analysis of kinetic data of $[M_2L_2](py)_2(H_2O)_2$ ($M = Ni$ or Cu)

This analysis was carried out for step II of the thermo-decomposition process of each complex.

The combined differential and integral methods were used for these analyses [4,5]. Here the differential equation is from Achar et al. [6] and the integral equation was modified by Coast and Redfern [7]. The most probable mechanism was selected among 19 kinetic functions which were numerically listed in the literature [8]. And every function has its $f(\alpha)$ differential and $g(\alpha)$ integral form, with which all original data (every value of $[d\alpha/dt]$) were analyzed. Thus, all 38 sets of data for each complex, including E, $\ln A$ and r, were obtained (which were submitted as supplementary materials).

Table 3
Thermal decompositions of the complexes

	$[Ni_2L_2](py)_2(H_2O)_2$			$[Cu_2L_2](py)_2(H_2O)_2$		
	Step I	Step II	Step III	Step I	Step II	Step III
Temperature (°C)	41–200	490	>900	52–172	424	703
Weight found	13.8	41.1	–	10.8	43.2	11.1
Losses calculated (%)	13.9	43.8	–	13.8	43.5	10.3

The results indicate that the two E values are approximately equal, so also are the two $\ln A$ values, and the linear correlation coefficients are best ($r \approx 1$) when the function number 6 was taken as the most probable mechanism function for $[Ni_2L_2](py)_2(H_2O)_2$. The same parameters were given for $[Cu_2L_2](py)_2(H_2O)_2$, but the mechanism function may be either number 6 or 4. In consideration of the similar thermal decompositions and the structures, the same function number 6 should be determined for both complexes.

The mechanism function number 6 is Zhuralev–Lesokin–Tempelman equation, $f(\alpha) = 1.5(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$ and $g(\alpha) = \{[1/(1-\alpha)]^{1/3}-1\}^2$, which belongs to a three-dimensional diffusion. Here $E = 138.7\ \text{kJ mol}^{-1}$ (taking arithmetic mean value of 137.32 and $140.16\ \text{kJ mol}^{-1}$ resulting from differential and integral method, respectively) and the mean $\ln A = 24.3$ for the Ni complex, and $E = 246.8\ \text{kJ mol}^{-1}$ (the mean value of 257.85 and $235.73\ \text{kJ mol}^{-1}$) and the mean $\ln A = 46.5$ for the Cu complex.

4. Supplementary materials

All bond lengths and angles, and some least-square planes have been submitted to the Cambridge Crystallographic Data Center, deposited with code CCDC 144279. Two tables on $a - (\mathrm{d}\alpha/\mathrm{d}t)$ and two tables on all calculated results, including 38 sets of values of E, $\ln A$ and r, for two complexes, respectively, have been submitted to the Editorial Office.

Acknowledgements

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