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Synthesis and properties of one-dimensional Ni(II) and Ni(II)Cu(II) complexes linked by hydrogen bond

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Abstract Four dithiooxalato (Dto) bridged one-dimensional Ni(II) and Ni(II)Cu(II) complexes $(Me_6[14]dieneN_4)Ni_2(Dto)_2$ (**1**), $(Me_6[14]dieneN_4)CuNi(Dto)_2$ (**2**), $(Me_6[14]aneN_4)Ni_2(Dto)_2$ (**3**), and $(Me_6[14]aneN_4)CuNi(Dto)_2$ (**4**), were synthesized. These complexes have been characterized by elemental analysis, IR, UV and ESR spectra. The crystal structure of complex **3** was determined. It crystallizes in the monoclinic system, space group C2/c with a = 2.2425(4) nm, b = 1.0088(2) nm, c = 1.4665(3) nm, β = 125.32(3)° ; Z = 4; R = 0.076, R_w = 0.079. In the complex, Ni(1) coordinates four sulphur atoms of two Dto ligands in plane square environment. Ni(2) lies in the center of macrocyclic ligand. For Dto ligand, two sulphur atoms coordinate Ni(1), and O(1) coordinates Ni(2) and forms weak coordination bond. O(2) is linked to N(2) of macrocyclic ligand through hydrogen bond.

Keywords: 1,2-dithiooxalato, nickel complex, one-dimensional complex, nickel-copper heteronuclear, complex, crystal structure, hydrogen bond.

The research and application of bridged polynuclear complexes is one of the most active fields in coordination chemistry. Design and synthesis of bridged polynuclear complexes are important tasks of modern coordination chemistry. It is very enticing in the inorganic biochemistry and molecule material chemistry. Nowadays, most of research work is focused on the donor atoms of the second period elements. However, there are a few studies in the field of bridged magnetic coupled complexes with the donors of the third period elements[1—6]. The reason for this is due to the instability and difficulty of purify in common methods for this kind of complexes. The preparation of samples with high purity for magnetic measurements and growth of single crystals are more difficult. As a donor atom, sulphur atom has a big atom radius, small negativity and empty 3d orbits. It can effectively delocalize the electrons of the bridged paramagnetic ions and transfer the magnetic interaction of paramagnetic ions. As a bridged ligand including sulphur atoms, Dto has variable coordination modes and strong ability of transferring electrons[7]. So far, there are a few Dto bridged complexes that were determined by the X-ray structural analysis.

In this paper, Dto and nitrogen-containing macrocyclic ligands are employed as bridged and terminal ligands, respectively. Four one-dimensional Ni(II) and Ni(II)Cu(II) complexes are synthesized and characterized by elemental analysis, IR and UV spectra. The ESR spectra are studied and the structure of complex **3** is determined.

1 Experimental

1.1 Reagent and instrument

5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetra-tetradecane were synthesized according to the literature[8]. Other reagents are analytical grade and used as received. Elemental analysis for C, H and N was carried out with a Perkin-Elmer Model 240 elemental analyzer. Metal contents were determined by EDTA titration. The IR spectra were recorded in the range of 600—4000 cm^{-1} on an IR-408 spectrophotometer in KBr discs. The electronic absorption spectra were performed in the range of 200—800 nm on a UV-2101 PC spectrophotometer. ESR spectra were carried out on the 200-SRC and JES-FE1XG (X band) Electron Spin Resonance spectrograph.

1.2 Preparation of complexes

1.2.1 Synthesis of the precursor complexes. Four macrocyclic complexes, $[Me_6[14]dieneN_4Ni]\cdot(ClO_4)_2$, $[Me_6[14]dieneNiCu](ClO_4)_2$, $[Me_6[14]aneN_4Ni](ClO_4)_2$, and $[Me_6[14]aneN_4Cu](ClO_4)_2$, were prepared with the literature methods[9—11]. $K_2[Ni(Dto)_2]$ was prepared according to the literature[12].

1.2.2 Synthesis of the complexes. 0.2 mmol $[Me_6[14]dieneN_4Ni](ClO_4)_2$ (118 mg) was dissolved in 20 mL water, and 25 mL water solution containing 0.2 mmol $K_2[Ni(Dto)_2]$ (75 mg) was added with stirring. Precipitates appeared at once. After having been stirred at 70℃ for 1 h, the mixture was filtered and the precipitates were washed with water and ether 2—3 times. The microcrystal products of complex **1** were dried in vacuum with P_2O_5. By the similar method, we used $[Me_6[14]dieneN_4Cu](ClO_4)_2$, $[Me_6[14]aneN_4Ni](ClO_4)_2$ and $[Me_6[14]aneN_4Cu](ClO_4)_2$ to take the place of $[Me_6[14]dieneN_4Ni](ClO_4)_2$, and the complexes **2**—**4** were prepared. Anal. Calc. for complex **1** ($C_{20}H_{30}N_4Ni_2O_4S_4$)(%); C 37.65, H 5.05, N 8.78, Ni 18.39; found (%): C 37.28, H 5.11, N 8.85, Ni 17.93. Anal. Calc. for complex **2** ($C_{20}H_{30}N_4CuNiO_4S_4$)(%): C 37.36, H 5.02, N 8.71, Ni 9.15，Cu 9.88；found (%): C 37.19，H 5.04，N 8.71，Ni 9.65，Cu 10.23. Anal. Calc. for complex **3** ($C_{20}H_{34}N_4Ni_2O_4S_4$)(%): C 37.41, H 5.65, N 8.72, Ni 18.28；found (%): C 37.17，H 5.69，N 8.58，Ni 18.87. Anal. Calc. for complex **4** ($C_{20}H_{34}N_4CuNiO_4S_4$)(%): C 37.12，H 5.61，N 8.66，Ni 9.07，Cu 9.82; found (%): C 36.97, H 5.66, N 8.51, Ni 8.42, Cu 9.17.

1.3 X-ray crystallography

The single crystal of complex **3** suitable for X-ray crystallography was obtained by recrystalization of DMSO many times. Intensity data for complex **3** was collected on an Enraf-Nonius CAD-4 four-circle diffractometer at room temperature fitted with graphite monochromatized

Mo-Kα radiation (λ = 0.071073 nm). The $\omega/2\theta$ scan technique was employed to measure data in each case up to a maximum Bragg angle of 25°. All data were corrected for LP factors, for the empirical absorption and the extinction. The crystal structure was solved by direct method. The other non-hydrogen atoms were determined with successive difference-Fourier syntheses. All data calculations were performed using SDF-PLUS program system on a PDP11/44 computer. The final refinement R = 0.076. R_w = 0.079. The relevant crystallographic data are given in table 1.

Table 1 The crystallographic data of complex **3**

Empirical formula	$C_{20}H_{34}N_4Ni_2O_4S_4$	β/(°)	125.32(3)
Formula weight	581.48	V/nm^3	1.783(1)
Crystal dimension	0.10 mm × 0.25 mm × 0.45 mm	Z	4
Crystal color	red	$\rho_{calc.}$/mg·m^{-3}	1.427
Temperature/K	299±1	F(000)	1224
Crystal system	monoclinic	θ_{max}/(°)	25
Space group	C2/c(#15)	Reflections measured	2631
a/nm	2.2425(4)	Independent reflections ($I > 3.00\sigma(I)$)	1872
b/nm	1.0088(2)	R	0.076
c/nm	1.4665(3)	R_w	0.079

2 Result and discussion

2.1 Synthesis of the complexes

The synthesis and measurement of this kind of complexes are very difficult because the sulphur-containing ligands and complexes are unstable and not easy to purify. As the sulphur-containing ligand, Dto has not only the above feature but also two negative charges. It is very easy to form precipitates with metal ion and difficult to obtain single crystals. In this paper, the unstable K_2Dto is replaced by the stable $K_2[Ni(Dto)_2]$ as the intermediate, and the nitrogen-containing macrocyclic complexes are employed as the terminal ligand. Four Dto bridged one-dimensional complexes are prepared and the single crystal of complex **3** is obtained. The complexes **2** and **4** are determined to be heteronuclear species by elemental analysis and ESR characterization.

2.2 X-ray crystal structure of complex 3

The crystal structure of complex **3** is shown in fig. 1. Atomic coordinates, selected bond distances and angles are given in tables 2 and 3, respectively.

In complex **3**, there are two symmetric centers of nickel atoms that form two units which are bridged by Dto. Ni(1) coordinates four sulphur atoms to form plane square coordination environment. All the atoms of Dto and Ni(1) lie in the same plane and Ni(1) locates in the center of the plane square. Ni(2) coordinates four nitrogen atoms of the macrocyclic ligand and two oxygen atoms (O(1) and O(1a)) which occupy the axial position. Ni(2) lies in the center of the distorted octahedron. The bridges ligand Dto bridges Ni(1) and Ni(2) through two sulphur atoms and one

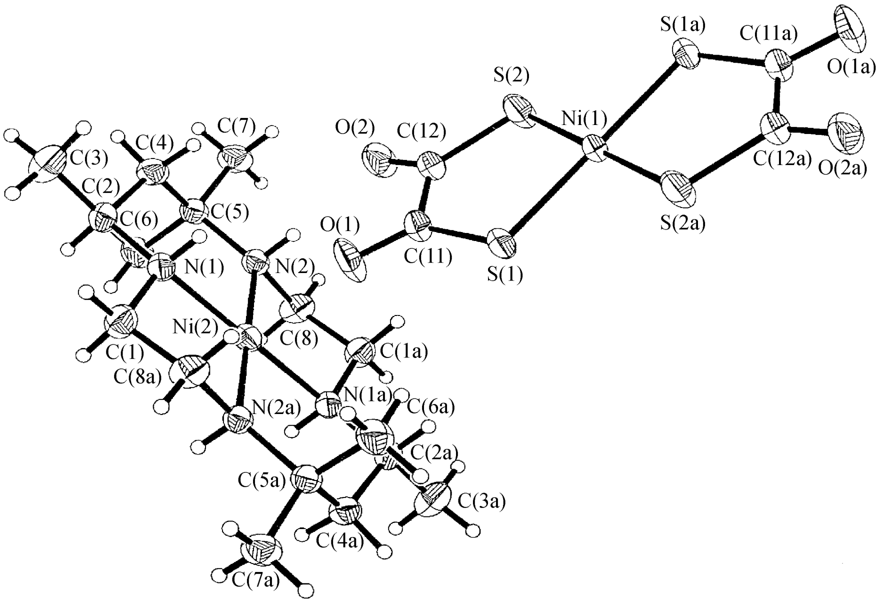

Fig. 1. Crystal structure of complex **3**.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for complex **3**

Atom	x	y	z	U_{eq}/nm^2
Ni(1)	0.5000	0.5000	0.5000	0.035(1)
S(1)	0.4279(1)	0.3390(1)	0.3963(1)	0.044(1)
S(2)	0.4632(1)	0.6262(1)	0.3557(1)	0.054(1)
C(11)	0.3744(1)	0.4033(3)	0.2641(2)	0.043(1)
C(12)	0.3946(2)	0.5395(3)	0.2431(2)	0.044(1)
O(1)	0.3204(1)	0.3477(3)	0.1850(2)	0.070(1)
O(2)	0.3601(1)	0.5802(2)	0.1465(2)	0.063(1)
C(1)	0.1281(2)	0.2204(3)	−0.0110(3)	0.048(1)
N(1)	0.1642(1)	0.3388(2)	−0.0148(2)	0.036(1)
C(2)	0.1142(1)	0.4398(3)	−0.0971(2)	0.041(1)
C(3)	0.0583(2)	0.4931(4)	−0.0789(3)	0.061(2)
C(4)	0.1603(2)	0.5546(3)	−0.0937(2)	0.043(1)
C(5)	0.2096(1)	0.5295(3)	−0.1326(2)	0.038(1)
C(6)	0.1661(2)	0.4803(3)	−0.2526(2)	0.053(1)
C(7)	0.2501(2)	0.6569(3)	−0.1216(3)	0.051(2)
N(2)	0.2652(1)	0.4247(2)	−0.0541(2)	0.034(1)
C(8)	0.3168(2)	0.3745(3)	−0.0787(3)	0.047(1)
Ni(2)	0.2500	0.2500	0	0.039(7)

oxygen atom. O(2) is linked to N(2) by the hydrogen bond. There are two chiral carbon atoms in the nitrogen-containing macrocyclic ligand, which have both *R* and *S* polymorphic configuration. The nitrogen-containing macrocyclic ligand is an internal compensation isomer. The whole complex structure is Dto-bridged one-dimensional chain structure as shown in fig. 2. The bond distances of coordinated Ni-S are 0.2173(1), 0.2182(1), 0.2173(1), and 0.2182(1) nm, respectively. They are in agreement with the data of Dto complexes reported in the literature. The bond distances of coordinated Ni-N are 0.2017(3), 0.2041(2), 0.2017(3), and 0.2041(2) nm, respectively. Both Ni(2)-O(1) and Ni(2)-O(1a) distances are 0.2423 nm. The hydrogen bond distance between O(2) and N(2) is 0.2035 nm. This kind of coordination mode of Dto has not been reported in the literature. Complex **3** is the first example of Dto bridged one-dimensional Ni(II) complex.

Table 3 Selected bond distance (nm) and angle (°) for complex **3**

Ni(1)-S(1)	0.2173(1)	S(1)-Ni(1)-S(2)	92.7(1)
Ni(1)-S(2)	0.2182(1)	Ni(1)-S(1)-C(11)	105.1(1)
S(1)-C(11)	0.1712(3)	Ni(1)-S(2)-C(12)	105.3(1)
S(2)-C(12)	0.1710(2)	N(1)-Ni(2)-N(2)	86.5(1)
N(1)-Ni(2)	0.2017(3)	N(2)-Ni(2)-N(1a)	93.5(1)
N(2)-Ni(2)	0.2041(2)		
N(2)-H(12)	0.0875		
Ni(2)-O(1)	0.2423		
O(2)-H(12)	0.2035		

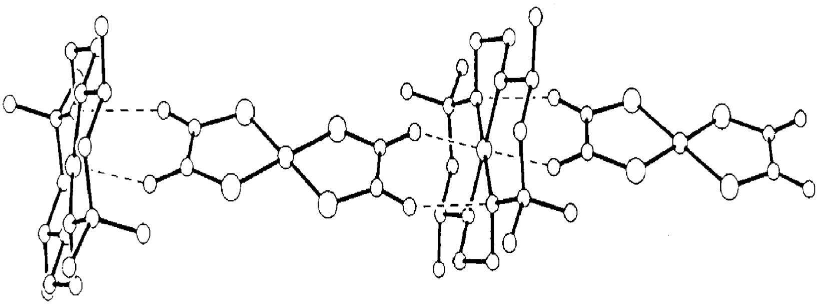

Fig. 2. One-dimensional chain of complex **3**.

2.3 Spectroscopic characterization of the complexes

2.3.1 IR spectra of the complexes. The IR spectra of complexes **1**—**4** are similar and the feature peaks appear at 1560, 1070, 938 and 1438 cm^{-1}, respectively. There is another peak appearing at 1650 cm^{-1} which attributes to the vibration absorption of the C$=$N bond for complexes **1** and **2**. The peak of 1438 cm^{-1} shows that the Dto bridges the two nickel atoms through both oxygen and sulphur atoms. This is agreement with the crystal result.

2.3.2 UV-Vis spectra of the complexes. The UV-Vis spectra of the four complexes and the nitrogen-containing macrocyclic ligand were measured in DMF solution. They are very similar to the spectra of $K_2[Ni(Dto)_2]$. The peak appearing at 302 nm attributes to n~π* change-transfer transition of the Dto ligand. There are two peaks appearing at 503 and 550 nm which belong to the d~d transition of $[Ni(Dto)_2]^{2-}$. No peaks can be observed as the Ni(II) and Cu(II) of the nitrogen-containing macrocyclic ligand. It is probably because the molar extinction coefficient of Ni(II) and

Cu(II) in the nitrogen-containing macrocyclic ligand is far smaller than that of $K_2[Ni(Dto)_2]$. Therefore, the absorption peak is covered by that of $[Ni(Dto)_2]^{2-}$.

2.3.3 Electron spin resonance spectra of the complexes. The ESR spectra of the complexes were measured at both room temperature and 110 K with powder samples and DMF solution. The spectra of complexes **2** and **4** are shown in fig. 3. Ni(1) is low spin with $S = 0$. No ESR signal is observed because the diamagnetic Ni(II) ion lies in the plane square center. Ni(2) lies in the enlonged octahedral center and the distance between Ni(2) and O(1) (or O(2)) is far, so no ESR signal is observed in complexes **1** and **3**. There is a single peak without superhyperfine splitting appearing at the solid spectra for the copper-containing complexes **2** and **4**. But the superhyperfine splitting of complexes **2** and **4** is observed in DMF solution spectra. The ESR parameters obtained from the spectra are listed in table 4.

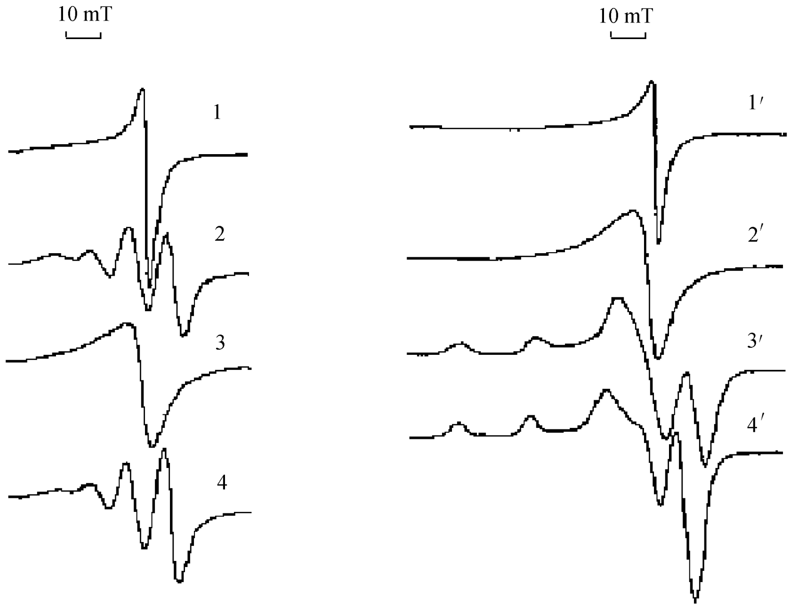

Fig. 3. ESR spectra of complexes **2** and **4**. 1, (Me$_6$[14]dieneN$_4$)CuNi(Dto)$_2$ powder, 298 K; 1′, (Me$_6$[14]dieneN$_4$) · CuNi(Dto)$_2$ powder, 110 K; 2, (Me$_6$[14]dieneN$_4$)CuNi(Dto)$_2$ solution, 298 K; 2′, (Me$_6$[14]aneN$_4$)CuNi(Dto)$_2$ powder, 110 K; 3, (Me$_6$[14]aneN$_4$)CuNi(Dto)$_2$ powder, 298 K; 3′, (Me$_6$[14]dieneN$_4$)CuNi(Dto)$_2$ solution, 110 K; 4, (Me$_6$[14] aneN$_4$) CuNi(Dto)$_2$ solution, 298 K; 4′, (Me$_6$[14]aneN$_4$)CuNi(Dto)$_2$ solution, 110 K.

Table 4 ESR data of complexes **2** and **4**

Serial	State	Room temperature			Low temperature (110 K)		
		$g_{//}$	$g_{\perp}$	g	$g_{//}$	$g_{\perp}$	g
2	powder	—	—	2.05	—	—	2.05
	solution	2.11	1.98	2.02	2.17	1.96	2.03
4	powder	—	—	2.06	—	—	2.06
	solution	2.10	2.00	2.03	2.17	1.98	2.04

3 Conclusion

The ligands and the complexes containing sulphur atom are unstable and not easy to purify. In order to overcome the disadvantage, the Dto and nitrogen-containing macrocyclic ligand are employed as the bridged and terminal ligands, respectively. Four Dto bridged complexes are synthesized and the single crystal of complex **3** is obtained by DMSO recrystalization. A new bridged mode of Dto is confirmed by X-ray structural determination of complex **3**. In the polynuclear Dto-bridged system, two sulphur atoms of the trans-bridged Dto coordinate one kind of metal ion, an oxygen atom of Dto bridges another kind of metal ion and the second oxygen links to nitrogen atom of macrocyclic ligand by hydrogen bond. The whole complex is of one-dimensional chain structure through hydrogen bond.

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