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Synthesis and Quantum Chemistry Study of Nitrogen-Containing Heterocyclic Ligands

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Six novel nitrogen-containing heterocyclic ligands were synthesized. The electronic structures of these ligands have been studied by using the density functional theory of quantum chemistry program package Gaussian98. All the geometry structures of these ligands have been optimized at the level of B3LYP/6-31G*. The analysis of Mulliken populations and the main composition and proportion of the frontier orbitals indicated that these nitrogen-containing heterocyclic ligands should have some capabilities to coordinate with metal ions and the active site of each ligand have been confirmed elementarily. Investigation found that the electron repelling group containing in N'N-bis(4-picolinaminde)-4,4-benzindine is in favour of increasing the electron densities of the coordination atoms.

Key Words: Synthesis, Density function theory, Heterocyclic ligands.

INTRODUCTION

In recent years, there was increasing interest in the supramolecular polymer assembly by the coordination bond, the intermolecular hydrogen bond and other week intermolecular interactions in the inorganic chemistry. Metal ions would react directly with the aromatic multicaboxylic acid[1–7] and 4,4′-bipyridine[8–11] to form the multi-central coordination compounds. In the studies of the biomolecules, the oxygen atom bridged multi-central coordination compounds were investigated widely[12–16]. In 1995, Yaghi *et al.*[17] synthesized $Cu(4,4'\text{-bpy})_{1.5}$-$NO_3(H_2O)_{1.25}$ which was provided with network structure by $Cu(NO_3)_2$ and 4,4′-bipyridine.

Besides 4,4′-bipyridine, pyridine and pyrazine are the simple ligands in common use. $AgBF_4$ reacts with pyrazine in different proportion in ethanol can get varies of polymers with different structures and constitutions. Mak *et al.*[18] has reported the synthesis of the three dimensional [CuSCN(bpa)].

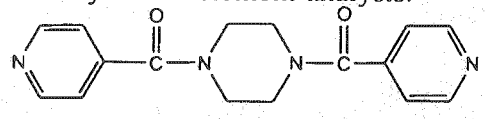
In this paper, the synthesis of six novel picolinamide-type nitrogen-containing heterocyclic ligands is reported. And the quantum chemistry study of these ligands was performed in using density function theory (DFT). The electronic structures and the coordination capabilities of these compounds are investigated in detail according to the quantum chemistry calculations.

EXPERIMENTAL

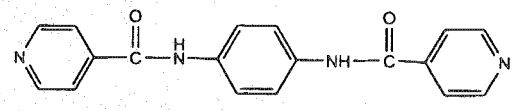
Synthesis of N,N′-bis(4-picolinamide)piperazidine (1)

To a solution of pyridine-4-carboxylic acid (0.1 mol) in pyridine (40 mL) was dropwised the solution of piperazidine (0.05 mol) in pyridine (20 mL) and triphenyl phosphite (0.1 mol), and the mixture stirred at 388 K for 5 h. After cooling to room temperature, the white deposition was precipitated and then filtered. The filtered deposition was recrystallized in from alcohol and water, and then N,N′-bis(4-picolinamide)piperazidine (1) was obtained after drying at room temperature for 24 h.

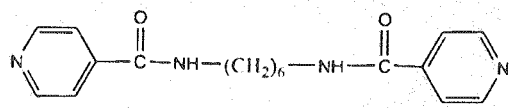
The synthesis procedures of other compounds were similar to N,N′-bis(4-picolinamide)piperazidine. What the different is changing piperazidine to the corresponding diamide. The structures of six novel ligands were performed by IR analysis and element analysis.



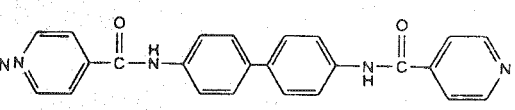
N,N′-bis(4-picolinamide)piperazidine (1)



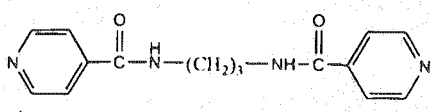
N,N′-bis(4-picolinamide)-*p*-phenylenediamine (2)



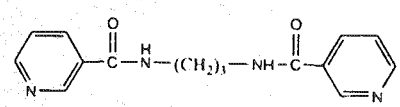
N,N′-bis(4-picolinamide)hexamethylendiamine (3)



N,N′-bis(4-picolinamide)biphenyldiamine (4)



N,N′-bis(4-picolinamide)-1,3-propanediamine (5)

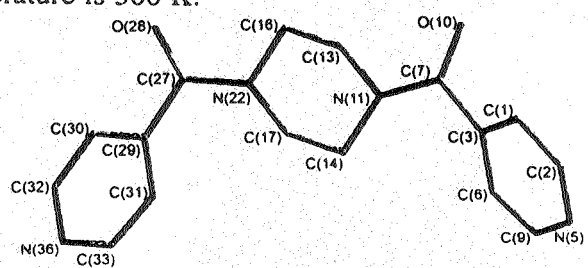


N,N′-bis(3-picolinamide)-1,3-propanediamine (6)

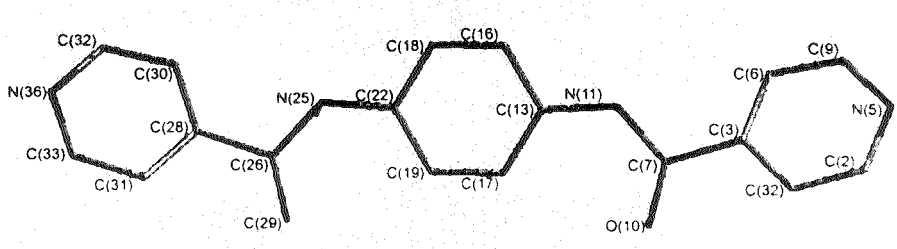
Fig. 1 Structures of the nitrogen-containing heterocyclic ligands

Quantum Chemistry Calculation

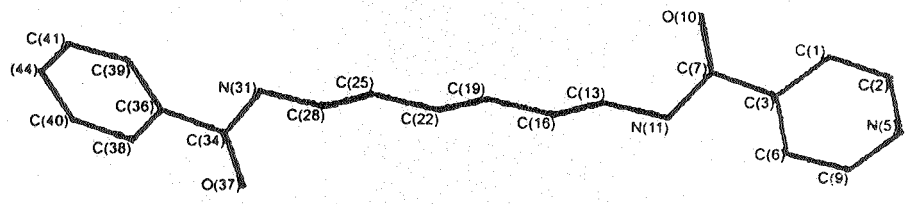
Computational quantum chemistry may be used as an analytical instrument in structure analysis. It has predictive power to assist synthesis and characterization. Because the crystal structures of the compounds were still not measured, the three-dimension structures of the compounds were built by the Chem3D package. And the MM2 force field was applied to search for the low energy conformations for each molecule[19], the step interval is 2.0 fs and the frame interval is 10 fs, the terminative step is 10000, the heating/cooling Race is 4.18 kJ (atom 7 ps) and the target temperature is 300 K.



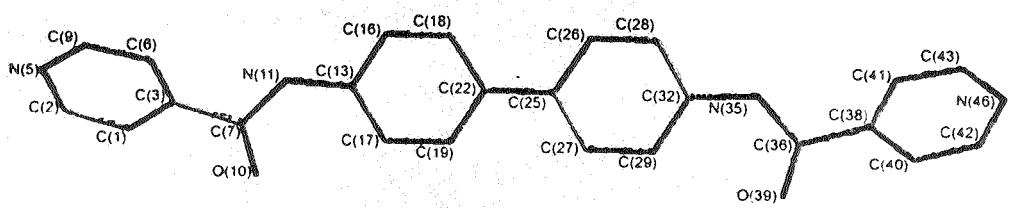
N,N′-bis(4-picolinamide)piperazidine (1)



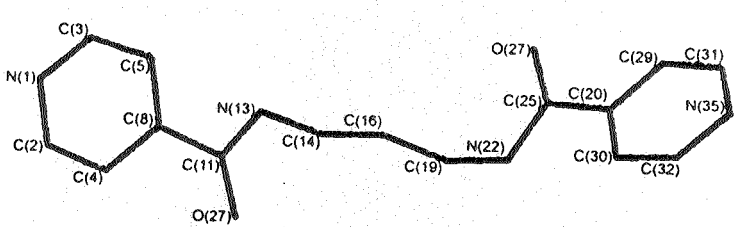
N,N′-bis(4-picolinamide)-*p*-phenylenediamine (2)



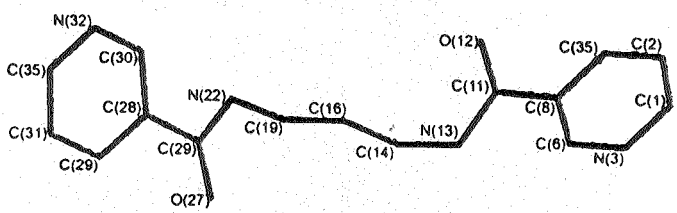
N,N′-bis(4-picolinamide)hexamethylendiamine (3)



N,N′-bis(4-picolinamide)biphenyldiamine (4)



N,N′-bis(4-picolinamide)-1,3-propanediamine (5)



N,N′-bis(3-picolinamide)-1,3-propanediamine (6)

Fig. 2. The lower energy conformations optimized by MM2 force field for the title compounds

Based on the lowest energy conformations (Fig. 2) calculated by MM2 force field, the compounds geometry structures were optimized at the Density Functional (DFT) level of theory using Beck 3 hybrid exchange(B3)[20] with Lee. Yang and Parr correlation[21] (B3LYP). The 6–31G* basis set was employed in this method. The frequency calculations for each molecule were carried out at 298.15 K and 1 atmosphere of pressure based on the optimized geometries calculated by B3LYP/6-31G*, and there were no imaginary frequencies appeared. So the

calculation results should be reliable. All of the quantum chemistry calculations was performed by using Gaussian98 package on Pentium IV PC.

RESULTS AND DISCUSSION

The energies and the main atomic electron density populations of the nitrogen-containing heterocyclic ligands

To obtain a better understanding of the title compounds stability, DFT calculations were used to examine the total energy of each molecule. The calculation results were summarized in Table-1.

TABLE-1
TOTAL ENERGIES OF THE NITROGEN-CONTAINING HETEROCYCLIC LIGANDS

Energy (A.U.)		Energy (A.U.)	
Compound 1	–988.7994	Compound 4	–1294.8846
Compound 2	–1063.8256	Compound 5	–950.7093
Compound 3	–1068.6512	Compound 6	–950.7115

The energies of **2**, **3** and **4** were lower than the energies of **1**, **5** and **6**, so the molecules of **2**, **3** and **4** would be more stable than **1**, **5** and **6** (Table-1). And the compound **4** has the lowest total energy among these compounds, so it would need more active energy to reactive with metal ions.

The analysis of Mulliken populations of the compounds **1**–**6** was based on the optimized geometry[22]. Main atomic electron density populations for the title compounds were given in Table-2.

TABLE-2
MAIN ATOMIC ELECTRON DENSITY POPULATION FOR THE NITROGEN-CONTAINING HETEROCYCLIC LIGANDS

Compound 1		Compound 2		Compound 3		Compound 4		Compound 5		Compound 6	
Atom	EC	Atom	EC	Atom	EC	Atom	EC	Atom	EC	Atom	EC
C3	0.0764	C3	0.0804	C3	0.0910	C3	0.0803	N1	–0.4001	N3	–0.4124
N5	–0.3999	N5	–0.3988	N5	–0.4008	N5	–0.3987	C8	0.0931	C11	0.5667
C7	0.5226	C7	0.5807	C7	0.5638	C7	0.5818	C11	0.5676	O12	–0.5313
O10	–0.4997	O10	–0.5007	O10	–0.5172	O10	–0.5012	O12	–0.5242	N13	–0.6167
N11	–0.4330	N11	–0.7399	N11	–0.6137	N11	–0.7383	N13	–0.6127	N22	–0.6167
N22	–0.4402	N25	–0.7399	N31	–0.6091	N35	–0.7383	N22	–0.6127	C25	0.5667
C27	0.5210	C26	0.5807	C34	0.5676	C36	0.5818	C25	0.5676	O27	–0.5313
O28	–0.4951	O29	–0.5007	O37	–0.5208	O39	–0.5012	O27	–0.5242	N32	–0.4124
N36	–0.4002	N36	–0.3988	N44	–0.4004	N46	–0.3987	N35	–0.4001		

EC: Electric charge.

There were mass negative electric charges on N and O of the compound **1–6**, so these atoms would have the capability to donate electrons to react with metal ions. For the compound **1**, O10 and O28 have more negative electric charges, so they would be the active position to coordinate with metal ions. For the compounds **2–6**, the amide nitrogen held more negative electric charges than other atoms (Table-2), so the amide nitrogen would have more stronger capability to coordinate with metal ions.

Main composition and proportion of frontier orbitals in compounds 1–6

According to the molecular orbital theory, the frontier molecular orbitals (HOMO, LUMO) and near orbitals have great influence upon the biological activity of compound[23–26]. The reaction between the active molecules mainly happens on the frontier molecular orbitals and near orbitals. Moreover, the front molecular orbital energies (E_{HOMO} and E_{LUMO}) and DELH ($E_{LUMO} - E_{HOMO}$) can also reflect the activities of the compounds. E_{HOMO} can be regarded as the measurement of the capability that the ligand supports electrons to metal ions. Higher E_{HOMO} mean the electrons of the ligand transferring to metal ions more easily. And DELH was correlated with the compounds stability. The energy difference of E_{HOMO} and E_{LUMO} is much bigger and the compound is more stable. On the contrary, smaller energy difference means that the compound is instable. Accordingly, the activity of the compound is much higher.

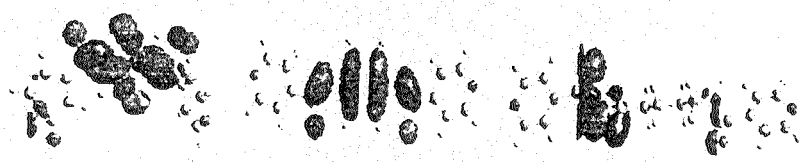
In order to investigate the relationship between the characteristic of the frontier orbital and the reactivity of the compounds **1–6**, the atomic orbital populations were calculated based on the optimized geometries. The front molecular orbital energies (E_{HOMO} and E_{LUMO}) and DELH ($E_{LUMO} - E_{HOMO}$) were listed in Table-3. We use the sum of square (SUMSQ) of each atomic orbital coefficients as the contribution of each atom to the molecular orbital, and calculated by nomalization method. Because the nitrogen-containing heterocyclic ligands **1–6** reacted with metal ions as electron donors, and the electron transfer between the title compounds and the metal ion mainly happened on the frontier orbital (HOMO) and the near occupied molecular obitals, so the main compositions and proportions of HOMO and the near occupied orbitals in each compound's molecule are listed in Table-4. The stereographs of the frontier molecular orbital HOMO of each acyclic polyether molecule are depicted in Fig. 3.

TABLE-3
FRONT MOLECULAR ORBITAL ENERGIES AND THE ENERGY DIFFERENCE ($E_{LUMO} - E_{HOMO}$) OF NITROGEN-CONTAINING HETEROCYCLIC LIGANDS

	Compd. 1	Compd. 2	Compd. 3	Compd. 4	Compd. 5	Compd. 6
E_{HOMO}/Hartree	–0.24685	–0.21521	–0.25310	–0.20880	–0.25492	–0.25065
E_{LUMO}/Hartree	–0.05542	–0.06830	–0.05508	–0.06764	–0.05676	–0.04752
DELH/Hartree	0.19143	0.14691	0.19802	0.14116	0.19816	0.20313

TABLE-4
MAIN COMPOSITIONS AND PROPORTIONS OF HOMO AND THE NEAR OCCUPIED OBITALS IN 1–6 (%)

Compound 1				Compound 2			
	HOMO-2	HOMO-1	HOMO		HOMO-2	HOMO-1	HOMO
C3	6.48	3.71	0.48	C3	4.69	4.32	0.77
N5	11.29	12.36	0.78	N5	15.77	12.39	0.37
O10	14.74	19.17	14.74	O10	13.26	12.96	5.93
N11	8.34	8.67	23.08	N11	3.40	3.07	15.36
N22	6.15	5.32	24.58	C13	0.35	0.32	14.15
O28	13.96	18.82	15.68	C22	0.35	0.32	14.15
C29	5.06	3.82	0.90	N25	3.40	3.07	15.36
O30	2.99	2.45	0.45	O29	13.27	12.96	5.93
N36	9.59	9.17	2.16	N36	15.77	12.38	0.37
Compound 3				Compound 4			
	HOMO-2	HOMO-1	HOMO		HOMO-2	HOMO-1	HOMO
C3	8.84	5.63	0.76	C10	1.38	5.88	3.66
N5	2.54	15.05	2.73	N11	0.32	15.82	9.18
O10	27.25	26.70	6.80	C13	0.15	5.31	9.71
N11	30.93	13.40	6.96	C16	11.68	5.14	3.60
N31	2.14	3.61	23.82	C22	0.26	7.80	9.11
O37	3.39	9.46	28.00	C25	0.26	7.80	9.11
N44	2.30	4.19	8.80	C32	0.15	5.31	9.71
				N35	0.32	15.82	9.18
Compound 5				Compound 6			
	HOMO-2	HOMO-1	HOMO		HOMO-2	HOMO-1	HOMO
N1	8.04	13.55	5.43	N3	10.88	10.93	0.17
C8	6.03	5.44	0.85	O12	19.89	20.87	10.89
O12	15.43	15.64	13.34	N13	5.38	6.18	28.85
N13	10.97	4.36	21.29	N22	5.73	5.88	28.75
N22	10.98	4.37	21.30	O27	21.14	19.62	10.87
O27	15.42	15.68	13.33	C28	5.50	5.20	0.97
C28	6.02	5.45	0.85	N32	11.55	10.26	0.18
N35	8.01	13.58	5.42				



Compound 1 Compound 2 Compound 3

Compound 4 Compound 5 Compound 6

Fig. 3. The stereographs of the frontier molecular orbitals HOMO of the nitrogen-containing heterocyclic ligands

For the compound **1**, the proportions of atoms O10, O28, N11 and N22 in HOMO (12.36, 13.14, 20.24 and 21.96%) were higher than other atoms as listed in Table-4, and these atoms all had negative charges (Table-2). So these atoms should the positions to donate electrons as reacting with metal ions. At the same time, N5 and N36 also had great negative charges (Table-2), though Table-4 showed that the atomic orbitals of these two atoms had little contribution to HOMO, N5 had 12.36% proportion in HOMO-1 and 11.29% proportion in HOMO-2, and N36 also had great proportion in near occupied orbitals, so N5 and N36 should also have some activities to react with metal ions.

The stereographs showed that the frontier molecular orbital (HOMO) of **2** was symmetrically distributed (Fig. 3). And the data of the main compositions and proportions of HOMO in Table-4 also illustrated it. Most HOMO of compound **2** was symmetrically distributed on the acylamide group and the centre benzene ring. The centre benzene ring is a full electron group; it would be good to increase the electron cloud density of N11 and N25. Accordingly, N11 and N25 should be easier to donate electrons to coordinate with metal ions. The DELH of compound **2** (Table-3) was 0.14691; it is lower than **1**, **3**, **5** and **6**. So compound **2** should be a highly active ligand among the nitrogen-containing heterocyclic ligands. Different from compound **2**, the HOMO of compound **3** was mainly distributed on N31 and O37 (23.82%, 28.00%). So these two atoms would be the most active positions to react with metal ions.

The frontier molecular orbitals (HOMO) of **4**, **5** and **6** were also symmetrically distributed on the acylamide group. For compound **4**, part of the HOMO was averagely distributed on the biphenyl group. Same as the compound **2**, biphenyl was a electron repulsion group; it had positive effect in increasing the electron cloud densities on the N atoms of the imine group. Accordingly, N11 and N35 of compound **4** were more easy to donate electrons to coordinate with metal ions

and the DELH of compound **4** is 0.14116; it illustrated that the energy difference of E_{HOMO} and E_{LUMO} of compound **4** is the smallest among the title compounds. So compound **4** would be a better ligand to coordinate with metal ions than others.

ACKNOWLEDGEMENTS

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