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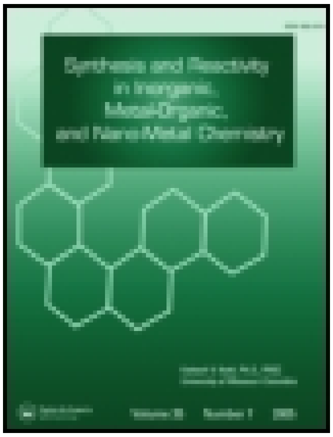

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Crystal Structure and Properties of the Enantiotopic Complex Constructed From Chiral Ligand H_2bpb, [Co $(H_2bpb)_2$ $(NCS)_2$ $(CH_3OH)_2$] (H_2bpb = 1, 2-Bis (3-pyridylcarboxamide)benzene)

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Synthesis, Crystal Structure and Properties of the Enantiotopic Complex Constructed From Chiral Ligand H_2bpb, [Co (H_2bpb)$_2$ (NCS)$_2$ (CH_3OH)$_2$] (H_2bpb = 1, 2-Bis (3-pyridylcarboxamide)benzene)

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A six-coordinating cobalt (•) complex, [Co(H_2bpb)$_2$ (NCS)$_2$ (CH_3OH)$_2$], where H_2bpb is 1,2-bis(3-pyridylcarboxamide) benzene, was prepared and characterized by IR spectrum and thermal analysis, and its crystal structure was determined by X-ray analysis. It crystallizes in the triclinic system with space group P-1 with a = 8.7005(9) Å, b = 9.6114(10) Å, c = 13.767(2) Å, α = 101.393(2)°, β = 93.185(2)°, γ = 114.5180(10)°, V = 1014.5(2) Å, Z = 1. Fluorescent and thermal properties of the complex were also investigated.

Keywords cobalt$^{(\bullet)}$ complex, crystal structure, fluorescent, thermal analysis.

INTRODUCTION

The syntheses of ligands based on 1,2-disubstituted benzene have attracted a great deal of attention, with a broad array of both acyclic and macrocyclic ligands reported.[1] In particular, diamides incorporating a –CO-NH-benzene-NH—CO—core based on 1,2-benzenediamine have been examined, with interest in these compounds extending to potential applications as diverse as asymmetric catalysis,[2] molecular receptors,[3] dendrite synthesis[4] and platinum(•) complexes with antitumor properties.[5] The carboxamide [–C(O)NH–] group, which is the primary structure of proteins, is all over in nature and an important ligand construction unit for coordination chemists.[6] In the control of molecular architectures, pyridine carboxamide ligands are used extensively.[7]

Coordination compounds containing the thiocyanate ligand are usually reported.[8] Thiocyanate plays the diverse role in the structural chemistry and the kinetics of the reactions.[9] Cobalt complexes are useful in highly selective catalytic oxidation reactions using molecular oxygen, as models for oxygenases, peroxydases or mono- and dioxygenases, for example, catalyzing the oxidation of phenols, alcohols, flavonoides, nitroalkanes, hydrazines or olefins. While extended coordination networks derived from pyridylamide ligands have been reported with the metal centers Ag(I), Au(I), Pd(II), and Pt(II),[10–12] the similar to Co(II) compounds have not been studied extensively. In the present communication, we have reported the synthesis of the complex [Co (H_2bpb)$_2$(NCS)$_2$(CH_3OH)$_2$] (H_2bpb = 1, 2-bis(3-pyridylcarboxamide)benzene) and turned our attention to characterization of the complex.

EXPERIMENTAL

Materials and Methods

Nicotinic acid was analytical pure grade from Alfa Aesar; phthalamine and other reagents were also analytical pure grade and purchased from TianJin Reagent Factory, used without further purification. The 1, 2-bis(3-pyridylcarboxamide)benzene (H_2bpb) was synthesized following a procedure reported previously[13] with a yield of 70%. Thionyl chloride and pyridine were redistilled. Melting points were taken on a XT-5 microscope melting point apparatus. IR spectra were recorded on a Nicolet IR-470 spectrometer from KBr pellets in range 4000–400 cm^{-1}. Crystallographic data was measured on a Bruker APEX-II area-detector diffractometer with Mo-Ka radiation (λ = 0.71073•). Thermal analysis curve was scanned in the range of 35–800•with argon atmosphere on STA 409 PC thermal analyzer. The fluorescence spectra were recorded in the solid state at room temperature on HITRCHI F-4500 fluorophotometer.

Synthesis of the Complex [Co(H_2bpb)$_2$(NCS)$_2$(CH_3OH)$_2$]

At room temperature, a clear DMF solution (5 mL) of H_2bpb (63.7 mg, 0.2 mmol) was slowly added to a methanol solution (10 mL) of $CoSO_4$ (56.2 mg, 0.2 mmol), then 5 mL solution

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TABLE 1
Crystallographic data and structure refinement for complex

Structural parameter	
Empirical formula	C40 H36 Co N10 O6 S2
M	875.84
Crystal group	Triclinic
Space group	P-1
a/Å	8.7005(9)
b/Å	9.6114(10)
c/Å	13.767(2)
$\alpha/^o$	101.393(2)
$\beta/^o$	93.185(2)
$\gamma/^o$	114.5180(10)
V/Å^3	1014.5(2)
D_c/g.cm^{-3}	1.434
Z	1
μ/mm^{-1}	0.586
Crystal size/mm^3	0.34 × 0.24 × 0.23
Reflns collected/Unique	7811/3769
$R1$, $\omega R2$[I>2σ(I)]	0.0298^a 0.0802^b

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b \omega R_2 = [\Sigma(||F_o| - |F_c||)^2/\Sigma\omega|F_o|^2]^{1/2}$

of potassium thiocyanate (19.4 mg, 0.2 mmol) in methanol was added to the above mixture with continuous stirring for 30 minutes, filtered. The filtrate was allowed undisturbed evaporation at ambient temperature, pink block crystals suitable for X-ray single crystal diffraction analysis were collected by being filtered and washed with methanol and acetone for one week later. Yield: 40%. IR (KBr, υ cm^{-1}): 3319 m, 3271 m, 2052 s, 1657 s, 1598 s, 1533 s, 1317 s, 1199 m, 1028 m, 918 m, 771m, 702 m.

X-Ray Structure Determination

Crystallographic data for the title compound was collected at 291(2) K on a Bruker APEX-II area-detector diffractometer with Mo-Ka radiation (λ = 0.71073●). Absorption corrections were applied by using SADABS. The structure was solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package.[14] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with commonly isotropic displacement factors and included in the final refinement by using geometrical restrains. Crystal data are summarized in detail in Table 1. Selected bond lengths and angles are put in Table 2.

RESULTS AND DISCUSSION

IR Spectra

In IR spectrum of the free ligand H_2bpb a band of medium intensity show at 3282 cm^{-1} and is recognized as the ν (NH).[15] The characteristic absorption bands at 1665, 1529 and 1283 cm^{-1} for H_2bpb are due to amide ●[mainly ν (C=O)], amide II [mainly ν (C–N)] and amide III [mainly δ(N–H)] vibrations, respectively. The complex have characteristic IR bands at 1657, 1533, 1316 cm^{-1}.[16] The amide ●[mainly ν (C=O)] did not disappear and trivially shift to 1657 cm^{-1}, which suggests that in the complex H_2bpb still is in keto-form and the non-coordination of this fragment. Comparing the corresponding bands of the complex with the free ligand, the obvious changes are found in amide ●and III vibrations. The amide I band shift to a lower frequency and the amide III band shift to a higher frequency. These facts may be explained by inter- and/or intra-molecular hydrogen bonding, and C=O group and N-H group did not take part in coordination with metal. The IR spectrum of the complex exhibits additional strong absorption bands at 2052 cm^{-1}, which should be ascribed to the occurrence of the SCN group.

TABLE 2
Selected bond distances (Å) and angles (deg) for cobalt(●) complex

Co(1)-N(5)	2.0814(16)
Co(1)-N(5)#1	2.0814(16)
Co(1)-O(3)	2.1011(14)
Co(1)-O(3)#1	2.1011(14)
Co(1)-N(1)	2.1855(14)
Co(1)-N(1)#1	2.1855(14)
N(5)-Co(1)-N(5)#1	180.0
N(5)-Co(1)-O(3)	88.50(7)
N(5)#1-Co(1)-O(3)	91.50(7)
N(5)-Co(1)-O(3)#1	91.50(7)
N(5)#1-Co(1)-O(3)#1	88.50(7)
O(3)-Co(1)-O(3)#1	179.999(1)
N(5)-Co(1)-N(1)	90.16(6)
N(5)#1-Co(1)-N(1)	89.84(6)
O(3)-Co(1)-N(1)	89.73(6)
O(3)#1-Co(1)-N(1)	90.27(6)
N(5)-Co(1)-N(1)#1	89.84(6)
N(5)#1-Co(1)-N(1)#1	90.16(6)
O(3)-Co(1)-N(1)#1	90.27(6)
O(3)#1-Co(1)-N(1)#1	89.73(6)
N(1)-Co(1)-N(1)#1	180.0

Symmetry transformations used to generate equivalent atoms: #1−x+2,−y+1,−z+1.

Described Crystal Structure of the Complex

The crystal structure of the complex, [Co (H_2bpb)$_2$(NCS)$_2$ (CH_3OH)$_2$], is showed in Figure 1, and selected bond distances and angles are listed in Table 2. The cobalt ion sits on a crystallographically imposed center. Two H_2bpb ligands as monodentate occupy two equatorial positions in trans through one pyridine nitrogen coordinating to Co (II), respectively. There are two thiocyanates on the position of equatorial plane through nitrogen atom also coordinating to Co (II)

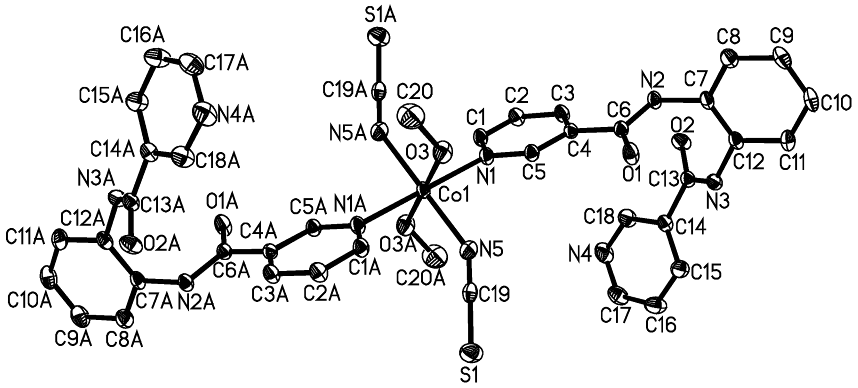

FIG. 1. Structure of $[Co(H_2bpb)_2(NCS)_2(CH_3OH)_2]$ with the atom labeling scheme (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

in trans, respectively. Axial positions are occupied by two oxygen atoms of two methanol molecules. Thus, the cobalt ion has an octahedral geometry, comprising CoN_4O_2 architectural coordination environment. The ligand bite angles of N1(py)-CoII-O3(methanol) are 89.73(6)°and 90.27(6)°, respectively; those of N5(thiocyanate)-CoII-O3(methanol) are 88.50(7)°and 91.50(7)°, respectively; those of N1(py)-CoII-N5 (thiocyanate) are 90.16(6)° and 89.84(6)° respectively (Table 2). The bond angles around Co(•) are fairly close to 90°, indicating a slight distortion of the octahedral coordination sphere. Mean value (2.1855(14) Å) of Co-N (py) lengths is appreciably longer than literature mean value (2.117(3) Å).[16] In this conformation, the plane I [C(7), C(8), C(9), C(10), C(11) and C(12)] make dihedral angles 91.8°and 145.1°with the plane II [N(1), C(1), C(2), C(3), C(4) and C(5)] and plane III [N(4), C(14), C(15), C(16), C(17) and C(18)], respectively. The plane II makes a dihedral angle 62.0° with the plane III (as in Figure 1). These dihedral angles reveal that all three aromatic rings are not coplanar to each other in the crystal structural unit.

Due to stereo-isomer influencing, the ligand H_2bpb, which coordinates cobalt (II) in trans form through one pyridine nitrogen atom exists in the chiral conformations ***A*** or ***B*** in solid state the complex, as shown in Figure 2. It is seen from Figure 1 that two H_2bpb and two thiocyanates coordinate to Co (II) in trans form, respectively, to form the complex having reverse center of symmetry and reverse plane of symmetry. So the chiral ligand H_2bpb coordinates to Co (II) to form a mononucleated enantiotopic complex.

The pyridine nitrogens N(3) and methanol hydroxyls form strong intermolecular hydrogen bonds (O(3)-H(3E)···N(4) = 2.762(2) Å). The molecules of the complex are linked together through solvent-mediated hydrogen bonding of the kind Co(•)... OH(Me)... N(Py) and form into 1D chain by slantly alternating bc plane (Figure 4). In 1D chains H_2bpb ligand donot

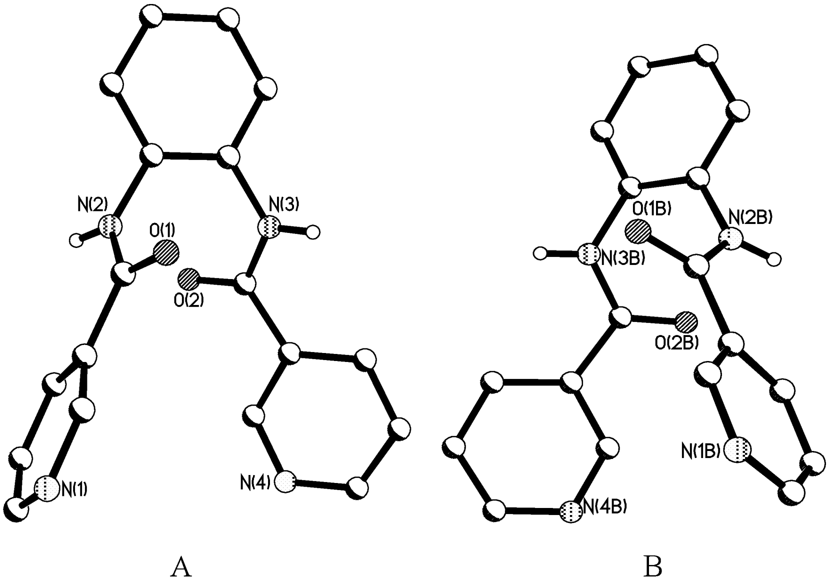

FIG. 2. Two chiral conformations of H_2bpb (hydrogen atoms have been omitted for clarity).

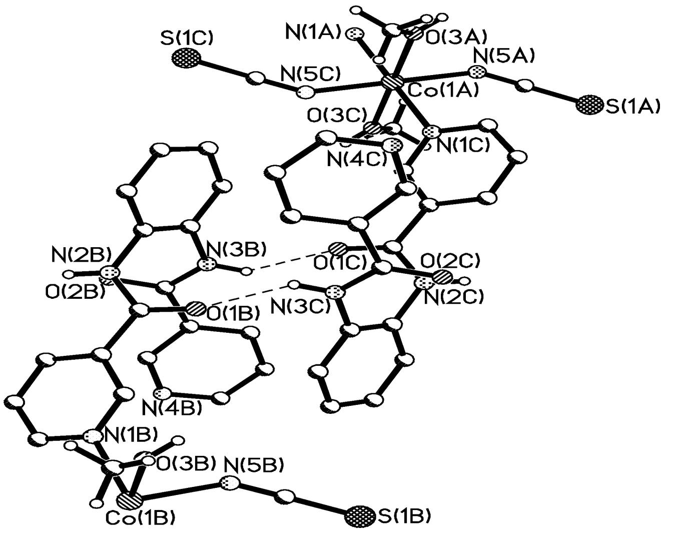

FIG. 3. Structure of the dimeric unit of [Co (H_2bpb)$_2$ (NCS)$_2$(CH_3OH)$_2$] with the atom labeling scheme. (parts of hydrogen atoms have been omitted for clarity).

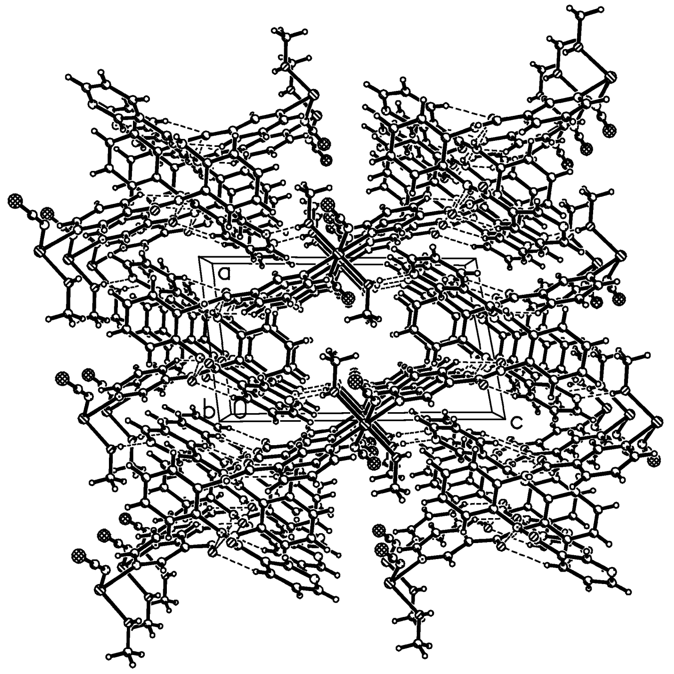

FIG. 5. The stereo drawings of the crystal packing of the complex. viewed along *b* axis.

parallel each other, which has a natural helicity. The solvate molecules of methanol play an important linkage part in the self-assembly process. Each ligand has four available NH and C=O groups available for intermolecular hydrogen bonding. Those 1D chians then self-assemble through intermolecular hydrogen bonds between carbonyl and amide groups (N(3)-H(3N)· · ·O(1) = 2.8789(19) Å) of adjacent molecules (Figure 3). Thus, in irregular direction a intricate three-dimensional network comes into being,[17]as shown in Figure 5.

Thermo-gravimetric Analysis (TG)

The thermal behavior of the complex under investigation was studied using the thermogravimetry (TG) and the DSC techniques. The DSC-TG curve of the complex (shown as in Figure 6) was scanned in the range of 30–800 •with argon atmosphere on STA 409 PC thermal analyzer. The thermal analytic data for the initial complex show a first endothermic weight loss of 7.09% between 157°C and 187°C with a DSC peak at 179 •, which corresponds exactly (calc. 7.32%) to the release of two molecules of coordinated methanol of the complex. After a loss of coordinated methanol, the TGA curve shows that the complex is stable up to 272°C. The intermediate [Co (H_2bpb)$_2$ (NCS)$_2$] is not thermally stable because a new endothermic decomposition starts at 272°C. The degradation of the ligand H_2bpb is a complicated process and takes place in the temperature range 272–800°C. The thermal decomposition process of the H_2bpb is not easy to understand because of unclear decomposition steps. The mass loss observed between 270 and 351•with a DSC peak

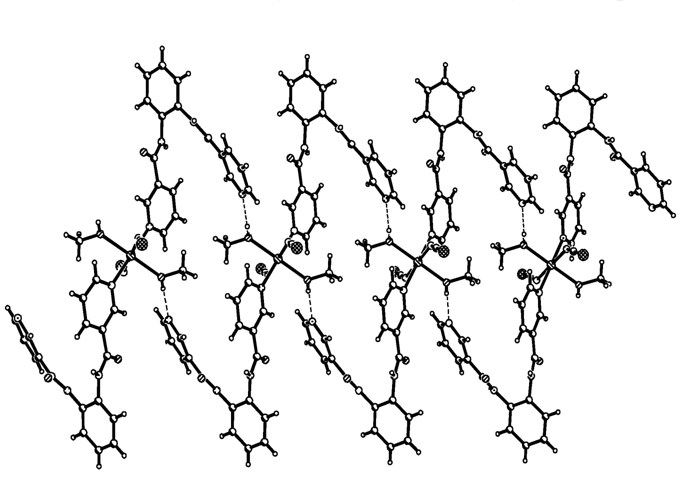

FIG. 4. One-dimensional ordering and of hydrogen-bond system [Co (H_2bpb)$_2$(NCS)$_2$(CH_3OH)$_2$].

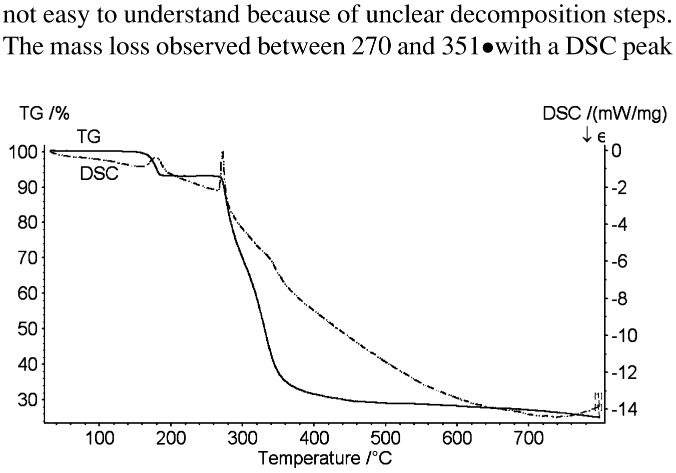

FIG. 6. TG/DSC curves for complex [Co (H_2bpb)$_2$(NCS)$_2$(CH_3OH)$_2$]. The curves were obtained in dynamic nitrogen atmosphere (approximately 50.0 ml.min^{-1}) and heating rate of 10 •.min^{-1}.

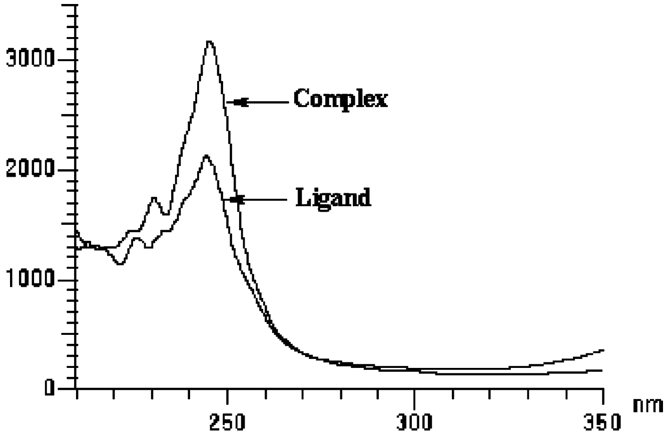

FIG. 7. The fluorescence excitation spectra of ligand and the complex in solid state.

at 272•is Δm = 55.14%. At higher temperatures (351–800•), a gradual mass loss totalizes 12.48% corresponding to the elimination of two molecule of SCN (calculated value = 13.25%). The total experimental mass loss value is 75.04% and the final residue at 800°C may be the buildup carbon and inorganic compound CoO.

Photoluminescent Properties

The fluorescence spectra of the ligand H_2bpb and the complex are determined in the solid state under the same measurement environment at room temperature on HITRCHI F-4500 fluorophotometer. The fluorescence excitation spectra of the ligand H_2bpb (λ_{max} = 244 nm) and that of the complex (λ_{max} = 245 nm) are illustrated in Figure 7. The emission spectra of the ligand and the complex upon excitation at the isosbestic point at 245 nm are plotted in Figure 8. Though the complex displays a evidently higher luminescence strength than ligand H_2bpb (λ_{max} = 389 nm), models and positions of their peaks are the same, which is likely attributed to the charge transfer of intra-ligand.

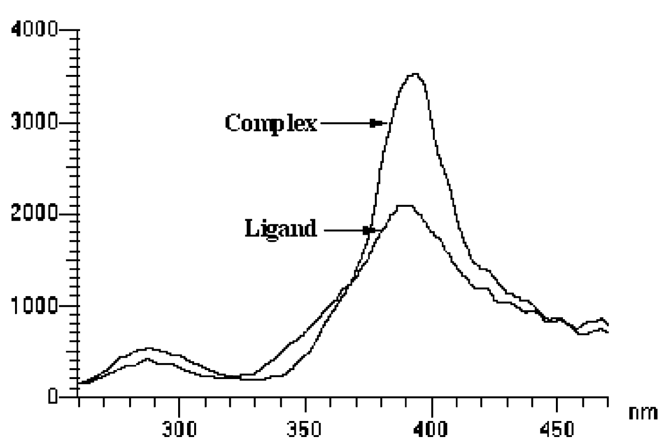

FIG. 8. The fluorescence emission spectra of ligand and the complex in solid state.

TABLE 3
Hydrogen bonds for L [Å and deg.].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(2)-H(2N)··· O(2)#2	0.86	2.07	2.8979(18)	161.7
N(3)-H(3N)··· O(1)#3	0.86	2.13	2.8789(19)	144.9
O(3)-H(3E)··· N(4)#4	0.79(3)	1.99(3)	2.762(2)	170(3)

Symmetry transformations used to generate equivalent atoms:
#1 −x+2,−y+1,−z+1 #2 −x+1,−y+1,−z #3 −x+1,−y,−z #4 x+1,y,z

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 609946 for the complex. Copies of these informations may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www:hppt://www.ccdc.cam.ac.uk).

REFERENCES

1. (a) J. B. Tara, J. E. Dana, J. P. Richard. Self-assembly using dynamic coordination chemistry and hydrogen bonding: mercury(II) macrocycles, polymers and sheets. Inorg. Chem., **2004,** 43, 5550–5557.
   (b) A. Mehdi, J. S. Kurt, M. Soraia. Synthesis and characterization of trans-[Co(III)(bpb)(amine)$_2$]X (X=NCS, ClO4). X-ray crystal structure of trans-[Co(III)(bpb)(pyrrolidine)$_2$]NCS·0.5H_2O containing intermolecular N-H. . . O=C hydrogen-bonding. Inorg. Chim. Acta, **2002**, 338, 19–26.
   (c) J. Lin, C. Tu, H. Lin, P. J. Jiang, J. Ding, Z. J. Guo. Crystal structure and superoxide dismutase activity of a six-coordinate manganese(III) complex. Inorganic Chem. Commun, **2003**, 6, 262–265.
   (d) J. B. Tara, J. E. Dana, C. J. Michael, J. Richard, Puddephatt ring-opening polymerization of gold macrocycles and self-assembly of a coordination polymer through hydrogen-bonding. Chem. Commun., **2003**, 2228–2229.
2. (a) D. A. Conlon, N. Yasuda. Practical method for the rhodium-catalyzed addition of aryl- and alkenylboronic acids to aldehydes. Adv. Synth. Catal., **2001**, 1, 343–350.
   (b) B. M. Trost, I. Hachiya, Asymmetric molybdenum-catalyzed alkylations. J. Am. Chem. Soc., **1998**, 120(5), 1104–1105.
3. (a)R. Collinson, T. Gelbrick, M. B. Hursthouse, J. H. R. Tucker. Novel ferrocene receptors for barbiturates and ureas. *Chem. Commun.*, **2001**, 555–556.
   (b) I. Huc, M. J. Krische, D. P. Funeriu, J. M. Lehn. Dynamic combinatorial Chemistry: Substrate H-bonding directed assembly of receptors based on bipyridine-metal complexes. *Eur. J. Inorg. Chem*, **1999**, 1415.
4. D. Epperson, L. J. Ming, G. R. Baker, G. R. Newkome, Paramagnetic Cobalt(II) as an NMR probe of dendrimer structure: mobility and cooperativity of dendritic arms. *J. Am. Chem. Soc.*, **2001**, 123, 8583–8592.
5. J. Y. Zhang, Q. Liu, C. Y. Duan, Y. Shao, J. Ding, Z. H. Miao, X. Z. You, Z. J. Guo. Structural evidence for the facile chelate-ring opening reactions of novel platinum(II)–pyridine carboxamide complexes. *J. Chem. Soc.*, Dalton Trans., **2002**, 591–597.
6. S. L. Jain, B. Pravat, H. L. Milton, M. Z. S. Alexandra, A. C. Joe, J. D. Woollins. New pyridine carboxamide ligands and their complexation to copper(II). X-Ray crystal structures of mono-, di, tri- and tetranuclear copper complexes. Dalton Trans **2004**, 862–871.

7. J. Hausmann, G. B. Jameson, S. Brooker, Control of molecular architecture by the degree of deprotonation: self-assembled di- and tetranuclear copper(II) complexes of N,N-bis (2–pyridylmethyl) pyrazine-2,3-dicarboxamide. Chem. Commun., **2003**, 2992– 2993.

8. (a) A. Mondal, C. Pariya, N. R. Chaudhuri, N. P. Nayak, A. K. Mukherjee, A. Ghosh. Syntheses of $[Ni_2(dien)_2(NCS)_4(H_2O)]$ and $[Ni(aepn)(NCS)_2]_n$ ((dien=bis(2-aminoethyl)amine and aepn=***N***-(2-aminoethyl)-1,3-propanediamine): single crystal structure analysis and thermal behaviour in the solid state. Polyhedron, **1997**, 16, 39–45.

(b) A. A. Khan, A. K. Saxena, K. Iftikhar, Mixed-ligand lanthanide complexes—X. Interaction of trivalent lanthanides with 1,10-phenanthroline and thiocyanate in alcohol. Polyhedron, **1997**, 16, 4143–4151.

(c) M. A. S. Goher, L. A. Alshatti, F. A. Mautner, A polymeric complex of copper (II) bridged simultaneously by tridentate glycinato and μ(N,S)-thiocyanato anions. Synthesis, spectral, structural and thermal properties of the complex [Cu(Glycinato)(NCS)(H2O)]. Polyhedron, **1997**, 16, 889–895.

(d) A. K. Mukherjee, S. Koner, A. Ghosh, N. R. Chaudhuri, M. Mukherjee, A. J. Welch, Isomerism in bis(diethylenetriamine)nickel(II) thiocyanate: synthesis, solid-state interconversion and X-ray crystallographic study of sym-*fac* and *mer* isomers. J. Chem. Soc., Dalton Trans. **1994**, 16, 2367–2371.

(e) G.S. Matouzenko, A. Bousseksou, S. Lecocq, P. J. Vankoningsbruggen, M. Perrin, O. Kahn, A. Collet, Spin transition in $[Fe(DPEA)(NCS)_2]$, a compound with the new tetradentate ligand (2-Aminoethyl)bis(2-pyridylmethyl)amine (DPEA): crystal structure, magnetic properties, and Mössbauer spectroscopy. Inorg. Chem. **1997**, 36, 2975–2981.

9. M. Amirnasr, K. J. Schenk, S. Meghdadi, Synthesis and characterization of trans-$[Co(III)(bpb)(amine)_2]$X (X=NCS, ClO4). X-ray crystal structure of trans-$[Co(III)(bpb)(pyrrolidine)_2]NCS\cdot/0.5H_2O$ containing intermolecular N-H. . . O=C hydrogen-bonding. Inorg. Chim. Acta, **2002**, 338, 19–26.

10. S. Muthu, J. H. K. Yip, J. J. Vittal, Coordination networks of Ag(I) and N,N - bis(3-pyridinecarboxamide)-1,6-hexane: structures and anion exchange. J. Chem. Soc. Dalton Trans. **2002**, 4561–4568.

11. Z. Qin, M. C. Jennings, R. J. Puddephatt, Self-assembly of polymer and sheet structures from palladium (II) complexes by hydrogen bonding between carboxamide substituents. Inorg. Chem. 2001, 40, 6220–6228.

12. T. J. Burchell, D. J. Eisler, M. C. Jennings, R. J. Puddephatt, Ring-opening polymerization of gold macrocycles and self-assembly of a coordination polymer through hydrogen-bonding. Chem. Commun. **2003**, 17, 2228–2229.

13. T. J. Burchell, D. J. Eisler, R. J. Puddephatt, Engineering silver (I) coordination networks through hydrogen bonding. Chem. Commun., **2004**, 944–945.

14. G. M. Sheldrick, SHELXL93, University of Göttingen, Germany, **1993**.

15. K. Gudasi, R. Vadavi, R. Shenoy, M. Patil, S. A. Patil, M. Nethaji, Transition metal complexes of a tridentate ligand bearing two pendant pyridine bases: The X-ray crystal structure of pentacoordinate copper(II) complex. Inorg. Chim. Acta, **2005**, 358, 3799–3806.

16. J. Wilson, M. Rabindranath, Synthesis, structure, and properties of monomeric Fe (II), Co (II), and Ni (II) complexes of neutral N-(aryl)-2-pyridinecarboxamides. Inorg. Chim. Acta, **2006**, 359, 4565–4573.

17. T. J. Burchell, D. J. Eisler, R. J. Puddephatt, Self-assembly using dynamic coordination chemistry and hydrogen bonding: mercury(II) macrocycles, polymers and sheets. Inorg. Chem., **2004**, 43, 5550–5557.