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Synthesis and characterisation of the Cd(II) complex of a hexadentate(N_4O_2) Schiff base ligand; IR, NMR and theoretical studies

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A new Cd(II) complex, Cd(L_{22pysa}), prepared from the template condensation of a previously known ligand $N(CH_2CH_2NH_2)_2(CH_2C_5H_4N)$, ($L_{22py}$), salicylaldehyde and $[Cd(NO_3)_2].4H_2O$ in equimolar ratio, has been characterised by IR and variable temperature ^{1}H NMR and ^{13}C NMR spectra. The gas-phase molecular structure of this complex was also studied by *ab initio* Hartree–Fock and DFT/B3LYP methods.

Keywords: hexadentate ligands; Schiff base complexes

There has been an increasing interest in the coordination chemistry of cadmium in recent years due to the increased recognition of its role in biological organisms,[1-5] as well as in molecular-based materials.[6-8] Recently we reported the synthesis and characterisation of a Cd complex that shows in its ^{1}H NMR spectrum that the signal of the imine proton has two clear satellites peaks (^3J = 42 Hz), with intensities in the ratio 1:6:1, due to coupling with a neighbouring $^{111/113}$Cd nucleus.[9] Obviously the observation of such coupling suggests that the Cd–N_{im} bond remains intact in solution. Although there are several reports of $^{111/113}$Cd–^{1}H heteronuclear coupling,[10-15] we could not find any clear pictures of the satellites similar to that reported in our research. Therefore we were interested to synthesise new Schiff base Cd complexes to study the latter interesting heteronuclear couplings. For this purpose, a previously known hexadentate tripodal Schiff base ligand,[16] bearing pyridinyl–phenolic groups (Fig. 1), was chosen to react with Cd ion. The reaction of zinc(II) and copper(II) metal ions with latter Schiff base ligand have been previously reported.[16,17] In the case of zinc ion, hydrolytic cleavage of one imine bond in the pro-ligand occurred, but in the case of copper ion a linear trinuclear complex was produced.

The Cd complex synthesised here was characterised by microanalysis, IR and NMR spectra. The gas-phase molecular structure of this complex was also studied by *ab initio* Hartree–Fock and DFT/B3LYP methods.

Experimental

Salicylaldehyde and its metal salt were obtained from Merck Company and were used without further purification. The asymmetrical tripodal ligand, $N(CH_2CH_2NH_2)_2(CH_2C_5H_4N)$ as its hydrochloride salt, L_{22py}.3HCl, was prepared by the literature method.[18] IR and NMR spectra were measured on Perkin–Elmer FT-IR GX, and Bruker FT-NMR 500Hz spectrometers respectively.

Computational methods

The geometry of the resulting complex, Cd(L_{22pysa}), in the gas phase were fully optimised at both the Hartree–Fock and DFT (B3LYP)[19] levels of theory using the Gaussian 98 set of programs.[20] At first, this complex was optimised using the standard LanL2MB basis set[21] and then the resulting structures were used for further calculations using a standard 3-21G* basis set for ligand atoms, and LanL2DZ for the metal ion.[22,23] The latter resulting structures were also used for similar calculations using the 6-31G* basis set for ligand atoms.[24] Therefore this complex was fully optimised with six different methods. Vibrational frequency analyses, calculated at the same level of theory, indicate that optimised structures are at the stationary points corresponding to local minima without any imaginary frequency. Calculations were performed on a Pentium-PC computer with a 2400 MHz processor. A starting molecular mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program.[25]

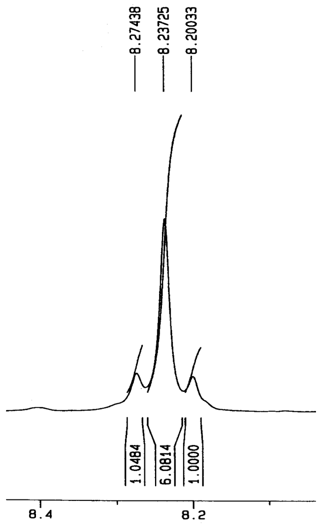

Fig. 1 The observed satellites in the ^{1}H NMR spectrum of compound **1** for CH=N hydrogen resonances. Note that the relative intensities of observed peaks are as (12.81 + 12.22)/2: 74.97: (12.81 + 12.22)/2 or *ca* 1:6:1.

Preparation of complex

[Cd(L_{22pysa})] (**1**, $C_{24}H_{24}N_4O_2Cd$)
This complex was prepared by a template condensation method. L_{22py}.3HCl (0.1 g, 33 mmol) and NaOH (0.039 g, 0.99 mmol) were mixed and heated under reflux for 1 hour in EtOH (15 cm^3) solution. Then NaCl, which formed on cooling, was filtered off. The filtrate was added to salicylaldehyde (0.08 g, 0.66 mmol) and the solution was stirred at 30-40°C for 1 h. Et_3N (0.17 g, 1.68 mmol) was added to the solution, then $Cd(NO_3)_2.4H_2O$ (0.114 g, 0.37 mmol) dissolved in MeOH (5 cm^3) was added. The mixture was stirred at 50–60°C for 1 h. The resulting white powder was washed with Et_2O. Yield: 0.024 g (14.1%) of **1**. Anal. Calcd. (Found) for $C_{24}H_{24}N_4O_2Cd$: C, 56.3 (55.7); H, 4.7 (4.8); N, 10.9 (10.3)%. IR (Nujol): 1634, 1596, 1572, 1540 ($\upsilon_{C=N}$ and $\upsilon_{C=C}$) cm^{-1}. ^{1}H NMR (500 MHz, DMSO, T = 292 K): δ 2.62 (t, 2H, 1-H_α), 3.02 (t, 2H, 1-H_β), 3.55 (t, 2H, 2-H_α), 3.68 (t, 2H, 2-H_β), 4.04 (s, 2H, *CH_2*-Py), 6.35 (s, 1H), 6.48 (s, 2H), 7.09 (m, 5H), 7.24 (s, 1H), 7.41 (d, 1H, J = 5 Hz), 7.82 (s, 1H), 8.23 (s, 2H, with two satellite peaks at ratio 1: 6: 1 relative to main signal, $^3J(^{111/113}Cd\text{-}^1H)$ = 37.0, 4-H), 8.71 (s,1H, H-Py). ^{1}H NMR (500 MHz, DMSO, T = 343 K): δ 2.68 (t, 2H, 1-$H_{-\alpha}$), 2.91 (t, 2H, 1-H_β), 3.60(m, 4H, 2-$H_{-\alpha}$ and 2-H_β), 4.04 (s, 2H), 6.35 (s, 1H), 6.48 (s, 2H), 7.09 (m, 5H), 7.24 (s, 1H), 7.41 (s, 1H), 7.82 (s, 1H), 8.23 (s, 2H, with two satellite peaks at ratio 1 : 6 : 1 relative to main signal, $^3J(^{111/113}Cd\text{–}^1H)$ = 37.0, 4-H), 8.71 (s,1H, H-Py). ^{13}C NMR (124 MHz, DMSO): δ 46.72 (C-1), 56.85 (C-2), 58.55 (C-3), 114.56, 120.94, 124.01, 124.24, 124.99, 133.31, 136.73, 136.90, 139.76, 150.89, 156.69 (aromatic rings), 171.13 (C-4).

Results and discussions

The [Cd(L_{22pysa})] complex was readily synthesised by the template condensation of neutralised L_{22py} tripodal ligand with salicylaldehyde and characterised by IR and ^{1}H NMR and ^{13}C NMR spectra. The absence of **a** pair of sharp υ(N–H) bands in

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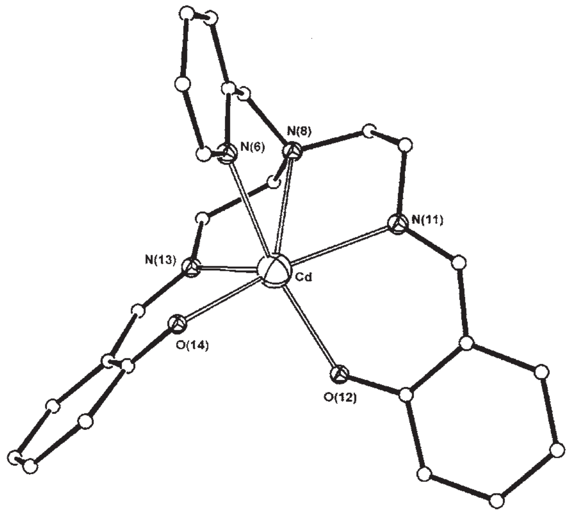

Fig. 2 Calculated molecular structure of compound **1** at the B3LYP level of theory, using standard 6–31G* basis set for ligand atoms and LanL2DZ for the metal ion. Hydrogen atoms are omitted for clarity.

the IR spectrum of the latter complex and presence of a series of bands at about 1634, 1596, 1572 and 1540 cm^{-1} related to $\upsilon_{C=N}$ and $\upsilon_{C=C}$, which are different from those of free ligand (1632, and 1589 cm^{-1}) is consistent with the existence of a coordinated imine group. The ^{13}C spectrum of this complex is completely consistent with its formulation and is similar to those of the free ligand except that, as expected, there are small shifts in the corresponding peaks. The ^{1}H NMR spectrum of this complex, in contrast to free ligand, shows the signal of the imine proton to have two satellite peaks ($^{3}J = 37.0$ Hz) with intensities in the ratio 1:6:1 (Fig. 1) due to coupling with neighbouring $^{111/113}$Cd at natural abundance (^{111}Cd, 12.81; ^{113}Cd, 12.22%). The very similar magnetogyric ratio of ^{113}Cd and ^{111}Cd, –5.93303 and –5.6720 × 10^{-7} rad/Ts, respectively, lead to satellite overlap at the resolution available. It should be noted that there are several reports of $^{111/113}$Cd–^{1}H heteronuclear coupling,[10-15] and we very recently published a clear picture of these satellites very similar to that shown in Fig. 1.[9]

It is very interesting that while the ^{13}C NMR spectrum of this complex at 292 K shows, similar to free ligand, two distinct methylene carbons for ethylene chains but its ^{1}H NMR spectrum at same temperature shows, in contrast to free ligand, two kinds of protons for each methylene group. While at 292 K there are four triplet peaks showing that dynamic exchange between the diasterotopic protons in resulting six-membered chelate rings are completely frozen out but at 343 K there are three peaks with slightly different chemical shifts. The latter observations confirm that proton topomerisation of methylene groups in the six-membered rings of this compound are impossible in room or lower temperatures. It should be noted that the study of the NMR spectra of this complex at higher temperature was not possible due to decomposition of this Schiff base complex in DMSO solution. Thus the IR and NMR data clearly confirm that the ligand is coordinated to Cd ion in this complex.

Ab initio and DFT studies

The geometry of compound **1** was also fully optimised with six different methods at both the Hartree–Fock (HF) and DFT/B3LYP levels of theory.

Selected calculated bond lengths and bond angles of this complex are given in Table 1. The results of different methods studied here are close to each other and show that the two imine nitrogens and two phenol oxygens as well as pyridine nitrogen and single tertiary nitrogen donor atoms, are arranged at apices of a significantly distorted octahedron (Fig. 2). The Cd–N and Cd–O bond lengths are in the normal range but the minimum and maximum bond angles are different with those expected for a regular octahedron structure.

The result of gas-phase theoretical studies shows that the ligand is strongly capable of encapsulating the Cd ion and is thus consistent with our experimental observations in solid and solution states for the [Cd(L_{22Pysa})] complex.

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Table 1 Selected calculated bond lengths (Å) and bond angles (deg) for compound **1**

	Computational level[a]					
	LanL2MB		3–21G* (LanL2DZ for Cd)		6–31G* (LanL2DZ for Cd)	
Bond lengths						
Cd–N(6)	2.416	**2.409**	2.440	**2.421**	2.542	**2.497**
Cd–N(8)	2.521	**2.489**	2.620	**2.606**	2.695	**2.684**
Cd–N(11)	2.268	**2.291**	2.322	**2.322**	2.375	**2.375**
Cd–N(13)	2.229	**2.258**	2.280	**2.288**	2.334	**2.339**
Cd–O(12)	2.116	**2.168**	2.145	**2.183**	2.181	**2.209**
Cd–O(14)	2.125	**2.176**	2.151	**2.197**	2.180	**2.212**
Bond angles						
N(6)–Cd–N(8)	69.8	**71.4**	67.8	**68.8**	65.9	**67.3**
N(6)–Cd–N(11)	87.6	**87.7**	90.3	**91.5**	86.8	**87.9**
N(6)–Cd–O(12)	149.9	**148.2**	161.31	**158.4**	155.3	**153.2**
N(6)–Cd–N(13)	101.2	**101.8**	93.1	**93.8**	95.5	**96.1**
N(6)–Cd–O(14)	83.6	**84.2**	81.	**81.0**	82.3	**82.8**
N(8)–Cd–N(11)	72.6	**73.6**	71.2	**72.0**	68.9	**69.8**
N(8)–Cd–O(12)	130.7	**132.0**	121.3	**125.2**	125.0	**127.6**
N(8)–Cd–N(13)	72.1	**73.0**	71.5	**72.3**	68.8	**69.8**
N(8)–Cd–O(14)	139.4	**142.1**	138.6	**139.5**	133.6	**135.5**
N(11)–Cd–O(12)	80.6	**81.3**	78.7	**79.4**	78.7	**79.2**
N(11)–Cd–N(13)	137.7	**139.9**	138.0	**139.0**	132.1	**133.9**
N(11)–Cd–O(14)	138.0	**135.4**	137.6	**137.1**	144.7	**143.5**
O(12)–Cd–N(13)	106.0	**105.8**	105.2	**105.9**	109.1	**109.8**
O(12)–Cd–O(14)	86.9	**82.9**	96.8	**92.3**	98.1	**93.7**
N(13)–Cd–O(14)	84.2	**84.6**	84.1	**83.9**	82.5	**82.3**

[a]The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold.

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