Tautomerism in complexes with neutral tetradentate Schiff base ligands: the X-ray structures of cadmium(II) nitrate complexes of bis(acetylacetone)-*m*-phenylenediimine and bis(acetylacetone)-*p*-phenylenediimine ☆

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Abstract

The Schiff base ligands bis(acetylacetone)-*m*-phenylenediimine (**L1**) and bis(acetylacetone)-*p*-phenylenediimine (**L2**) can be made to coordinate to Cd(II) without deprotonation. The products have the stoichiometries $Cd(L1)_2(NO_3)_2$ and $Cd_2(L2)_3(NO_3)_4$. Characterization by X-ray crystallography reveals polymeric structures in which Cd is eight-coordinate in the former and seven-coordinate in the latter. The nitrate groups are bidentate. The Schiff base ligands coordinate to Cd only through oxygen atoms and function as bridging bidentate keto-amine tautomers such that the NH···O hydrogen bonding networks present in the free ligands are preserved.

Keywords: Cadmium; Tetradentate; Quadradentate; Schiff-base; Polymeric

1. Introduction

Coordination complexes involving tetradentate (quadradentate) Schiff base ligands, abbreviated H_2SB, have been studied extensively for more than 50 years [1,2]. Theoretically this type of ligand can exist in the three tautomeric forms shown in Scheme 1. Typical R-groups have been –Me, –Ph (i.e., ketones), –OMe, –OEt (esters), and –NHR (a secondary amide). The most common backbones (BB) have been straight alkyl chains containing 2 to 12 CH_2 groups, short branched alkyl chains (e.g., ligands derived from 1,2-diamino-propane), and *o*-, *m*-, and *p*-phenyl linkers [1–3].

Previous IR and NMR studies on these ligands have indicated that they exist predominantly (if not entirely) as the keto-amine (or ketamine) tautomer, based on bands in the 3200 cm^{-1} region assigned to the ν(N–H) stretch and on chemical shifts in the δ 8.4–12.6 ppm region assigned to an N–H moiety [4–8]. Although very few of these ligands have been studied in the solid state using X-ray crystallography, available information, such as the structure of bis(benzylacetone)ethylenediimine (R = Ph, BB = –CH_2CH_2–), does confirm the presence of only the keto-amine tautomer [9].

Of the several methods known for making Schiff base complexes, the most effective one begins by synthesizing and isolating the ligand. Divalent metal ions (primarily Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and VO^{2+}) are commonly used because the ligands lose two protons and coordinate as divalent anions, thus forming neutral complexes. The Schiff base is reacted in a 1:1 mole ratio with the appropriate metal salt using methanol or ethanol solvent. Typically, acetate or hydroxide salts are used to deprotonate the ligand [1,2]. Alternatively, triethylamine can be used as the base [10], or sodium or potassium

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☆ It is customary in the literature to name tetradentate Schiff bases as their keto-imine tautomers even though they actually exist as keto-amine tautomers (vide infra). The CAS nomenclature for these ligands as keto-amine tautomers are 4,4'-*m*-phenylenedinitrilo)di-3-penten-2-one and 4,4'-(*p*-phenylenedinitrilo)di-3-penten-2-one, respectively.

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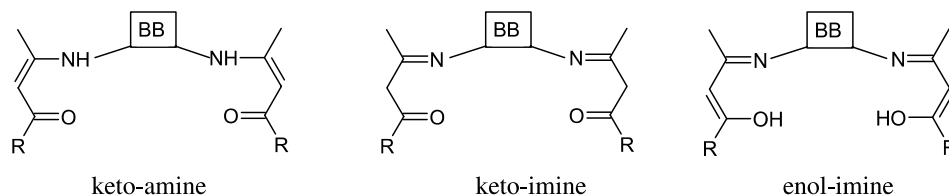
Scheme 1. Tetradentate Schiff base tautomers.

metal can be employed in methanol or ethanol to generate methoxide or ethoxide ions which then serve as the base [11,12]. Surprisingly few X-ray structural studies have been reported on these complexes. Two prominent examples are the structures of bis(acetylacetone)ethylenediiminatooxovanadium(IV) [13] and bis(benzylacetone)ethylenediiminatocobalt(II) [14]. The coordinated ligand in both complexes is essentially in the keto-amine form, absent the N–H hydrogens.

Interestingly, there have been a few complexes reported in which the tetradentate Schiff base ligand does *not* lose its protons and coordinates as a neutral species. This latter category of complexes has driven the work described here. In order to synthesize these complexes, non-basic anions (e.g., NO_3^-, Cl^-, ClO_4^-, and SO_4^{2-}) have been used and no additional bases (such as Et_3N) were added. Reactions are normally carried out at ambient temperatures since heating often causes deprotonation of the ligands. Proposed structures have been inferred almost exclusively from IR data. Unfortunately, IR may not be an effective diagnostic tool in trying to distinguish between a v(O–H) of a coordinated enol-imine tautomer or a v(N–H) of a coordinated keto-amine tautomer. It also appears that the interpretation of IR evidence regarding the mode of ligand coordination in this series of complexes has been somewhat inconsistent. What follows is a relatively complete list of the stoichiometries, proposed structures, and supporting IR evidence of complexes with neutral Schiff base ligands like those in Scheme 1:

(1) $ReOCl_3(H_2SB)$ and $Re_2O_2Cl_6(PPh_3)_2(H_2SB)$, where H_2SB has R = –Me and BB = $-CH_2CH_2-$ [15]. In the former, the Re is proposed to be six-coordinate where the Schiff base is thought to function as a bidentate ligand coordinating as the enol-imine tautomer through its two nitrogen atoms only. A strong, broad IR band at 3250 cm^{-1} was assigned to the v(O–H) stretch. In the latter, each Re is proposed to be six-coordinate with the Schiff base functioning as a bidentate bridging keto-amine ligand coordinated only through the oxygen atoms. A sharp, medium-strength IR band at 3220 cm^{-1} was assigned to the v(N–H) stretch. While the proposed structures are partially based on the number of available coordination sites on the Re, one might question assigning two very similar IR bands to an O–H in one case and an N–H in the other.

(2) $[UO_2(H_2SB)X_2]$ complexes where $X^- = NO_3$, Cl, I, $1/2SO_4$ and H_2SB has R = –Me or –Ph and BB = $-CH_2CH_2-$, $-CH_2CH(Me)-$, $-(CH_2)_3-$, or $-(CH_2)_6-$ [16,17]. It was noted that the linear UO_2^{2+} ion typically coordinates four, five or six additional donor atoms in its equatorial plane. If the tetradentate H_2SB Schiff base takes four of these positions, up to two positions remain for the coordinated anions. It was determined by IR that SO_4^{2-} was bidentate, and that NO_3^- was either monodentate [17] or bidentate [16]. Two bidentate nitrate ions occupy four coordination sites, leaving insufficient sites for the Schiff base to function as a tetradentate ligand. All complexes exhibit an IR band around 3150 cm^{-1}, interpreted by Mahanta and Dash [17] as v(O–H) of an enol-imine tautomer and by Kim et al. [16] as either v(O–H) of an enol-imine or v(N–H) of a keto-amine tautomer. Even when ample sites are available, squeezing a tetradentate ligand into four adjacent equatorial coordination positions with bite angles of about 60° does not seem that likely. In addition, regarding the ligand with a $-(CH_2)_6-$ backbone, it was shown recently that Schiff base ligands with backbones of five or more CH_2 groups form dimeric rather than monomeric structures with copper(II) [18]. These issues raise questions about the actual structure of the uranyl complexes.

(3) $[M(H_2SB)X_2]$ and $[M(H_2SB)]X_2$ complexes where $M^{2+} = Co$, Cu, Cd, or Hg, $X^- = Cl$, Br, I, SCN, NO_3, or ClO_4, and H_2SB has R = –NHPh and BB = $-CH_2CH_2-$ [19]. It is proposed that the complexes are monomeric with the ligand coordinating as the tetradentate keto-amine tautomer based on the presence of an IR band in the 3270–3230 cm^{-1} region assigned to v(N–H) of the ethylenediamine backbone. While this assignment seems reasonable, the situation is complicated by the presence of an amide N–H as well.

(4) Mixed metal complexes of the type $[CuZnCl_4(H_2SB)(MeOH)_2]$ where H_2SB has R = –Me and BB = $-(CH_2)_n-$ with $n = 6, 7, 8, 12$ [20]. These have been proposed to be dimeric complexes with both metal ions six-coordinate, two chloride bridges between Cu and Zn, one terminal chloride and one terminal MeOH on each metal, and the Schiff base ligand bridging between the two metal centers (bidentate on each), as the keto-amine tautomer. The presence of IR bands in the 3439–3424 cm^{-1} and the 1579–1584 cm^{-1} regions were assigned to the v(N–H) and δ(N–H) vibrations, respectively. The

former band seems a little uncharacteristic for an N–H moiety.

(5) $[Co_2Cl_2(H_2SB)_2]Cl_2$ and $[M_2Cl_4(H_2SB)_2]$ where $M^{2+} = Cu$ or Zn, and H_2SB has R = –Me and BB = *m*-Ph, *p*-Ph, or biphenyl [21]. These complexes are proposed to be dimeric, with five-coordinate cobalt and six-coordinate copper and zinc, and with each Schiff base ligand bridging the two metal centers (bidentate on each). A strong, broad IR band in the 3200–2900 cm^{-1} region in the ligands and the complexes was attributed to hydrogen-bonded N–H groups, again suggesting the presence of the keto-amine tautomer. One wonders, however, if the steric constraints imposed by some of these backbones would allow formation of simple dimers.

With IR bands being assigned over a wide but similar range to $v(O–H)$ or $v(N–H)$, and with proposed structures that include bidentate or tetradentate enol-imine tautomers in some cases and tetradentate or bridging bidentate keto-amine tautomers in others, the actual mode of coordination of the Schiff bases in these complexes seems quite uncertain. Our original plan was to resynthesize some of the complexes reported by Mahaptra and Pujari [19], Mishra and Upadhyay [20] and/or Aggarwal and Narayana [21] with the intention of growing high quality crystals and determining the structures of these complexes using X-ray crystallography. Unfortunately, in many cases we were unable to acquire pure identifiable products by the procedures described. Purity and solubility issues prevented our obtaining crystals appropriate for crystallography experiments. At this point we chose to work with two ligands reported by Aggarwal and Narayana [21], bis(acetylacetone)-*m*-phenylenediimine and bis(acetylacetone)-*p*-phenylenediimine, and to use $Cd(NO_3)_2$ as the metal salt in hopes of improving the solubility and purity of the products, and to provide a metal center with which we might be able to study the complexes by NMR should quality crystals not be forthcoming. We report here the X-ray structures of the two ligands and their cadmium(II) nitrate complexes.

2. Experimental

2.1. Synthesis of ligands

The ligands bis(acetylacetone)-*m*-phenylenediimine (**L1**) and bis(acetylacetone)-*p*-phenylenediimine (**L2**) were prepared with slight modifications of the procedure described previously [21]. A 2:1 mole ratio of acetylacetone and *m*- or *p*-phenylenediamine were refluxed overnight in methanol. Products, obtained by evaporating the solvent, were recrystallized from benzene and were verified by their melting points and proton NMR spectra.

L1: m.p.: 136–137 °C. ^1H NMR (CDCl$_3$/TMS): δ 12.49 (s, 2H, NH), 7.30 (t, 1H, aromatic), 6.93 (m, 2H, aromatic), 6.86 ($\sim$s, 1H, aromatic), 5.21 (s, 2H, C=CH), 2.10 (s, 6H, CH$_3$CO–), 2.02 (s, 6H, CH$_3$C(N)=C). X-ray quality crystals were grown from benzene.

L2: m.p.: 178–180 °C. ^1H NMR (CDCl$_3$/TMS): δ 12.47 (s, 2H, NH), 7.04 (s, 4H, aromatic), 5.20 (s, 2H, C=CH), 2.10 (s, 6H, CH$_3$CO–), 2.00 (s, 6H, CH$_3$C(N)=C). X-ray quality crystals were grown from benzene.

2.2. Synthesis of cadmium complexes

Initial syntheses utilized a 1:1 mole ratio of $Cd(NO_3)_2$ and the Schiff base ligand since the anticipated products were $[Cd(L)(NO_3)_2]_n$ dimers or polymers. After discovering that the actual stoichiometry of the products were $[Cd(L1)_2(NO_3)_2]$ (**I**) and $[Cd_2(L2)_3(NO_3)_4]$ (**II**), the complexes were resynthesized as follows.

A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (for **I**, 0.28 mmol, for **II**, 0.41 mmol, each in 5 ml of absolute ethanol and 5 ml of triethylorthoformate) was added dropwise over a 5 min period to **L1** or **L2** (0.56 mmol of **L1** or 0.61 mmol of **L2**, each in 5 ml of absolute ethanol, 5 ml of triethylorthoformate, and 3 ml of chloroform). The solutions were warmed and stirred for 10 min. In the case of **II** the product precipitated in about 5 min; in the case of **I** the solution was allowed to evaporate and the resulting oil was triturated with diethyl ether to obtain the solid product. The products were filtered, washed with diethyl ether, and air dried.

I: yield, 78%; dec. pt., 192 °C; elemental analysis, Calc. (found) for C$_{32}$H$_{40}$N$_6$O$_{10}$Cd: C, 49.20 (49.41), H 5.16 (5.03), N 10.76 (10.83)%; X-ray quality crystals were obtained from absolute ethanol.

II: yield, 45%; dec. pt. 235 °C; elemental analysis, Calc. (found) for C$_{48}$H$_{60}$N$_{10}$O$_{18}$Cd$_2$, C, 44.69 (44.59), H, 4.69 (4.72), N, 10.86 (10.84)%; X-ray quality crystals were grown from THF/hexane vapor diffusion.

2.3. Spectroscopic methods

^1H NMR spectra of **L1** and **L2** were obtained in CDCl$_3$/TMS with a Varian INOVA 400 MHz instrument. IR spectra were obtained using a Nicolet 510 FT-IR with a thunderdome solid-sampling attachment.

2.4. X-ray crystallography

X-ray data on all four compounds were acquired at ambient temperature using a Siemens/Bruker AXS P4 four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Initial solutions for **L1**, **L2**, and **I** were obtained by direct methods while the Cd in **II** was found via the Patterson heavy-atom method [22]. The remainder of each structure was

Table 1
Crystal data and structure refinement

Compound	**L1**	**L2**	**I**	**II**
Molecular formula	$C_{16}H_{20}N_2O_2$	$C_{16}H_{20}N_2O_2$	$C_{32}H_{40}CdN_6O_{10}$	$C_{48}H_{60}Cd_2N_{10}O_{18}$
Formula weight	272.34	272.34	781.10	1289.86
Crystal description	colorless plate	colorless parallelepiped	yellow pillar	yellow needle
Crystal size (mm)	$0.40 \times 0.37 \times 0.14$	$0.32 \times 0.28 \times 0.15$	$0.32 \times 0.20 \times 0.18$	$0.58 \times 0.10 \times 0.06$
Temperature (K)	297	298	297	297
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$Pbcn$	$P2_1/n$
Unit cell dimensions				
a (Å)	16.578(2)	5.492(1)	17.091(3)	9.070(2)
b (Å)	8.1830(9)	6.896(1)	14.062(2)	20.689(6)
c (Å)	10.953(2)	10.213(2)	14.699(2)	15.077(3)
α (°)	90	78.39(1)	90	90
β (°)	100.05(1)	79.78(2)	90	100.58(2)
γ (°)	90	89.78(2)	90	90
Volume (Å³)	1463.1(3)	372.7(1)	3532.7(9)	2781.2(12)
Z	4	1	4	2
D_{calc} (g cm⁻³)	1.236	1.213	1.469	1.540
$F(000)$	584	146	1608	1316
μ (mm⁻¹)	0.082	0.081	0.681	0.844
Max/min transmission	0.989/0.958	0.988/0.964	0.885/0.797	0.948/0.601
θ-range for data collection (°)	2.50–24.99	3.02–25.00	1.88–25.00	2.40–25.02
Index ranges	$-19 \leqslant h \leqslant 19$	$-6 \leqslant h \leqslant 6$	$0 \leqslant h \leqslant 20$	$-10 \leqslant h \leqslant 10$
	$0 \leqslant k \leqslant 9$	$-7 \leqslant k \leqslant 8$	$0 \leqslant k \leqslant 16$	$0 \leqslant k \leqslant 24$
	$0 \leqslant l \leqslant 12$	$0 \leqslant l \leqslant 12$	$0 \leqslant l \leqslant 17$	$0 \leqslant l \leqslant 17$
Reflections collected	3686	1753	4397	6403
Independent reflections/R_{int}	2572/0.0262	1315/0.0234	3120/0.0382	4891/0.0437
Data/restraints/parameters	2571/0/189	1312/0/95	3117/0/230	4890/0/352
Goodness of fit on F^2	1.085	1.157	1.109	1.076
$R1$, $wR2$ $[I = 2\sigma(I)]$[a,b]	0.0476, 0.1216	0.0588, 0.1525	0.0415, 0.0836	0.0512, 0.1083
a, b values in weighting[b]	0.0765, 0.1613	0.0758, 0.1513	0.0393, 0.0000	0.0594, 0.0000
Largest different peak/hole (e Å⁻³)	0.222/−0.218	0.194/−0.165	0.312/−0.313	0.730/−0.628

[a] $R1 = \sum \|F_o| - |F_c\|/ \sum |F_o|$.
[b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

developed by Fourier difference maps [22]. Data were corrected for absorption using the semi-empirical method XABS2 [23]. Refinements were performed by full-matrix least-squares on F^2 [22]. All non-hydrogen atoms were refined anisotropically. For **L1**, **L2**, and **I**, hydrogens on the nitrogen atoms were found via Fourier difference maps and refined; for **II** the three N–H hydrogens were added in ideal positions (N–H, 0.86 Å; $U_H = 1.2U_{attached\ N}$) and not refined. All hydrogens on carbon atoms were added in ideal positions (for aromatic and vinyl H's, C–H, 0.93 Å, $U_H = 1.2U_{attached\ C}$; for methyl groups, C–H, 0.96 Å, $U_H = 1.5U_{attached\ C}$). In all four structures, methyl groups were treated as symmetrically disordered. Crystallographic data are summarized in Tables 1 and 2, and thermal ellipsoid plots [22] are shown in Figs. 1–4. Additional details are available in Section 4.

3. Results and discussion

As outlined in the latter part of Section 1, IR spectroscopy does not appear to be an effective diagnostic tool for determining the mode of ligand coordination in complexes with neutral tetradentate Schiff base ligands. Thus, our goal was to prepare several representative complexes and determine their structures using X-ray crystallography.

3.1. NMR and crystallographic determination of ligand tautomers

Figs. 1 and 2 show the solid-state structures of **L1** and **L2**, respectively. The hydrogen atoms on N(1) and N(2) were found via Fourier difference maps, demonstrating the presence of keto-amine tautomers. Selected bond lengths and angles are given in Table 2. There is clearly a sp² center at C(3); the C=O bond lengths are typical of a ketone and are shorter than the C–N bonds, suggesting less double bond character in the latter; the C(3)–C(4) bonds are shorter than the C(2)–C(3) bonds, suggesting more vinyl character in the C(3)–C(4) region. In other words, these are classical keto-amine structures. The N–H bonds, which are in the 0.82–0.95 Å range, are oriented toward the nearest oxygen atom approximately

Table 2
Selected bond lengths (Å) and angles (°)

	L1	**L2**	**I**	**II**
Bond lengths				
C(2)–O(1)	1.246(3)	1.247(3)	1.255(5)	1.263(8)
C(15)–O(2)	1.244(2)		1.256(5)	1.267(8)
C(18)–O(3)				1.266(8)
C(2)–C(3)	1.421(3)	1.407(4)	1.399(6)	1.387(10)
C(14)–C(15)	1.419(3)		1.399(6)	1.386(10)
C(18)–C(19)				1.405(9)
C(3)–C(4)	1.361(3)	1.375(4)	1.373(6)	1.397(10)
C(13)–C(14)	1.368(3)		1.368(6)	1.376(9)
C(19)–C(20)				1.370(9)
C(4)–N(1)	1.355(3)	1.332(3)	1.343(5)	1.317(9)
C(13)–N(2)	1.356(3)		1.337(6)	1.341(8)
C(20)–N(3)				1.330(8)
N(1)–H(01)	0.95(3)	0.82(3)	0.81(4)	0.86[a]
N(2)–H(02)	0.86(2)		0.79(4)	0.86[a]
N(3)–H(03)				0.86[a]
O(1)···H(01)	1.84(3)	2.02(3)	1.94(4)	1.952
O(2)···H(02)	1.95(2)		2.02(4)	1.948
O(3)···H(03)				1.968
Cd–O(1)			2.342(3)	2.275(5)
Cd–O(2 or 2A)			2.284(3)[b]	2.246(5)[c]
Cd–O(3)			2.434(3)[d]	2.260(5)
Cd–O(4)			2.581(4)[d]	2.388(6)[d]
Cd–O(5)				2.407(6)[d]
Cd–O(7)				2.412(6)[d]
Cd–O(8)				2.391(6)[d]
Bond angles				
N(3)–Cd–N(3A)			172.9(2)[e]	
N(4)–Cd–N(5)				140.0(3)
O(1)–Cd–O(2A)			82.2(1)	109.7(2)
O(1)–Cd–O(1A)			86.8(1)[e]	
O(2A)–Cd–O(2B)			116.0(2)[e]	
O(1)–Cd–O(3)				86.2(2)
O(2A)–Cd–O(3)				164.1(2)

[a] N–H bonds in **II** were not found in the Fourier map; they were placed at ideal positions and not refined.
[b] O(2A) is generated from O(2) by the symmetry operation $1 - x$, $1 - y$, $-z$.
[c] O(2A) is generated from O(2) by the symmetry operation $1.5 - x$, $0.5 + y$, $1.5 - z$.
[d] Nitrate Cd–O bonds.
[e] These angles are bisected by the crystallographic twofold axis through the Cd.
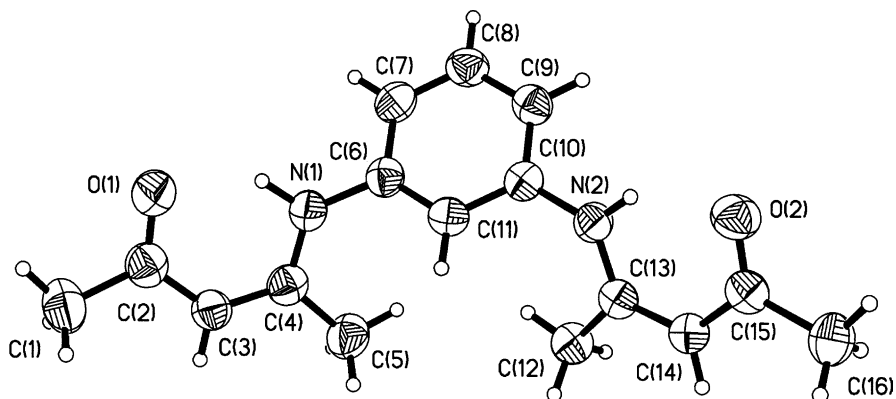

Fig. 1. Thermal ellipsoid plot at the 50% level for **L1**. Disordered methyl groups are not shown.
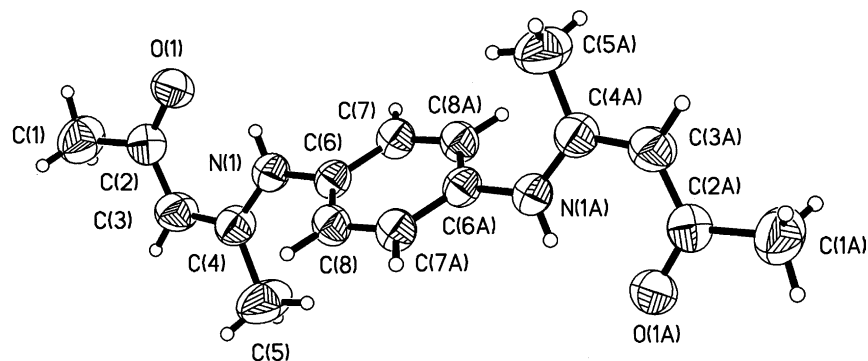
Fig. 2. Thermal ellipsoid plot at the 50% level for **L2**. Disordered methyl groups are not shown.
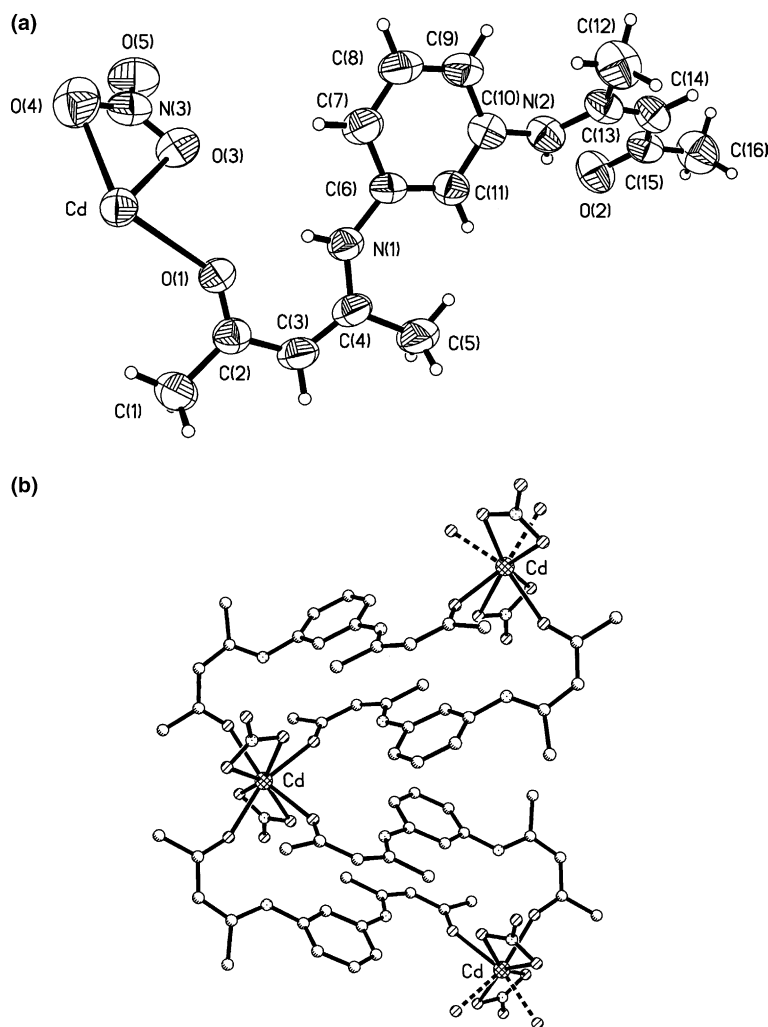

Fig. 3. (a) Thermal ellipsoid plot at the 50% level of the asymmetric unit of **I**. Disordered methyl groups are not shown. (b) Polymeric structure of **I**; hydrogen atoms are omitted for clarity.

1.84–2.02 Å away, establishing a substantial hydrogen-bonding interaction.

It would be difficult to elucidate the correct tautomer from the IR spectra of **L1** and **L2**. The hydrogen-bonded N–H bands are extremely weak and broad, spanning from about 3700 to 2700 cm^{-1} with the center somewhere between 3400 and 2900 cm^{-1}. There is only a difference of 1% transmittance between the peak center and the baseline. Undoubtedly this region includes the C–H vibrations as well. The ring C–C stretching mode
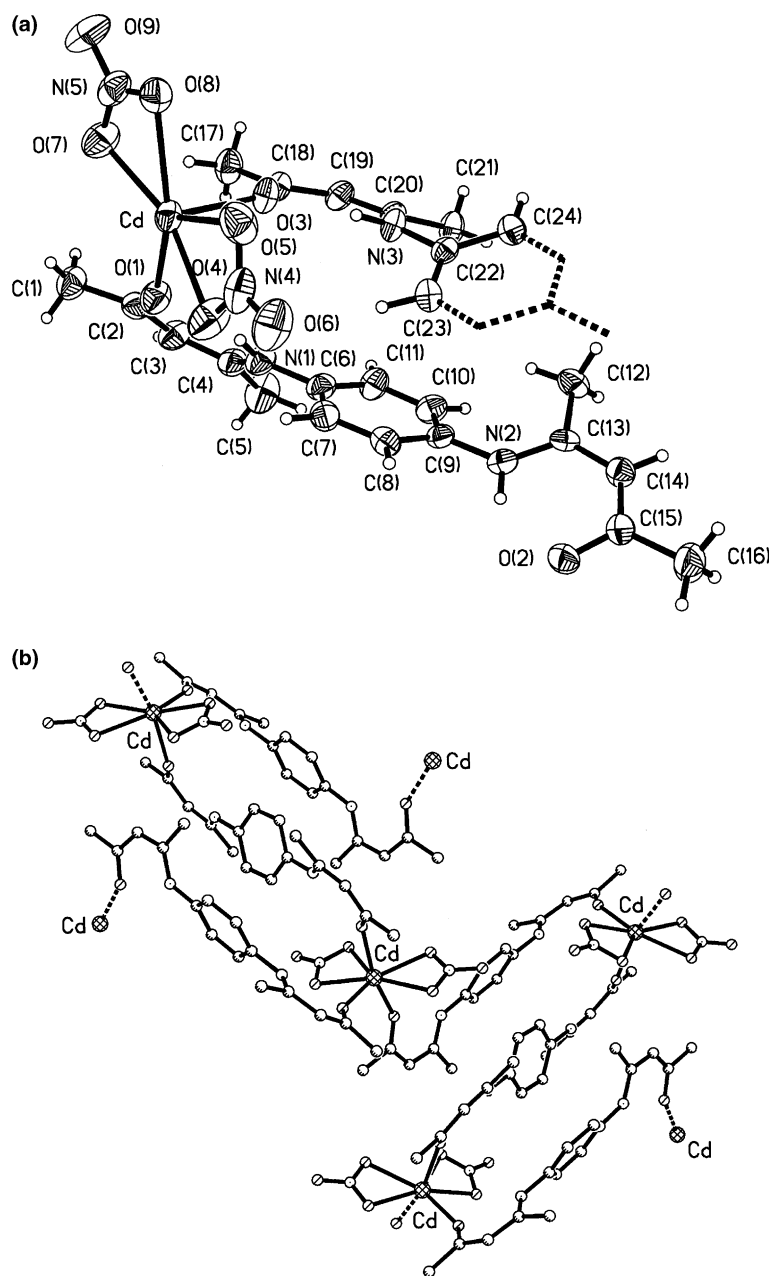
Fig. 4. (a) Thermal ellipsoid plot of the asymmetric unit of **II**. For clarity, ellipsoids are shown at the 30% level and disordered methyl groups are not shown. (b) Polymeric structure of **II**; hydrogen atoms are omitted for clarity.

shows up clearly as a strong band about 1565 cm^{-1} but the carbonyl stretch does not stand out clearly; a weak band about 1610 cm^{-1} is assigned to that mode.

NMR evidence (see Section 2.1) confirms the presence of only the keto-amine tautomer in chloroform solution. The resonance at about δ 12.5 is assigned to the hydrogen-bonded N–H moiety. This resonance is farther downfield than seen in many other Schiff base ligands (δ 8.4–12.6) [5–8]. The resonances about δ 5.2 are consistent with a vinyl center at C(3)–C(4).

In the solid state, Schiff base **L2** sits on a crystallographic inversion center making the two halves of the molecule equivalent. The C(1)–C(2)–O(1)–C(3)–C(4)–

N(1)–C(5) arm in **L1** and **L2** (and the corresponding C(12)–C(16) arm in **L1**) are quite planar, which facilitate the hydrogen-bonding interaction. These units, however, are not coplanar with the phenyl ring. In **L1**, the dihedral angles between the arms and the ring are 50.78(6)° and 49.79(6)°, while in **L2** the corresponding angle is 56.3(2)°. As will be seen shortly, these angles change rather dramatically when the ligands coordinate to cadmium.

3.2. Structures of the cadmium complexes

Neither complex in this study has the 1:1 metal:ligand stoichiometry as expected based on the reported

complexes of cobalt, copper, and zinc with these ligands [21]. Complex **I** has the stoichiometry of Cd(**L1**)$_2$(NO$_3$)$_2$; the atomic numbering scheme is shown for the asymmetric unit in Fig. 3(a) and the extended polymeric structure is shown in Fig. 3(b). Complex **II** has a stoichiometry of Cd$_2$(**L2**)$_3$(NO$_3$)$_4$; the atomic numbering scheme is shown for the asymmetric unit in Fig. 4(a) and the extended polymeric structure is shown in Fig. 4(b). In both of these structures, the Schiff base functions as a bridging bidentate ligand, bonding to Cd only though oxygen. The ligands remain in their keto-amine forms: the nitrogen atoms still have their respective hydrogens and while there are minor changes in various bond lengths (see Table 2), the classical keto-amine structure is maintained. In fact, the NH$\cdots$O hydrogen bonding interactions are preserved because the C(1)–C(5) and C(12)–C(16) arms retain their planarity.

In **I** (see Fig. 3) each Cd is eight-coordinate with four individual ligands and two bidentate nitrate ions in the coordination sphere. The crystallographic inversion operation $1 - x$, $1 - y$, $-z$ generates a symmetry equivalent oxygen, O(2A), which coordinates to the primary Cd shown in Fig. 3(a). In addition, Cd sits on a twofold axis which generates the second nitrate from the first, and the third and fourth ligands from the first two. The nitrates adopt an approximately *trans* geometry with a N–Cd–N angle of 173° but they are turned 62.3(2)° from one another. The four ligand oxygen donors form a highly distorted equatorial plane with O–Cd–O angles of 82–116° (see Table 2). Each Cd is connected by two ligands to its nearest neighbors, forming a double-strand chain structure in which there is a crystallographic inversion center between the two strands. There are some dramatic changes in the aforementioned dihedral angles. One arm remains in a similar orientation as in the free ligand (47.4(2)° versus the original of ≈50°) while the other arm becomes almost coplanar with the ring with a dihedral angle of 7.1(2)°. The phenyl rings of the two ligands connecting a given pair of neighboring Cd atoms are exactly parallel due to the presence of the inversion center, but they are offset from one another and thus do not overlap in a face-to-face stacking arrangement.

II (see Fig. 4) sits on an inversion center located in the middle of the ring partially defined by C(22)–C(23)–C(24). While there are similarities between the structures of **I** and **II**, there are also significant differences. In **II** only one ligand connects each pair of neighboring Cd atoms, forming more of a single-strand chain structure than the double-strand structure seen for **I**. Each Cd is seven-coordinate with three individual ligands and two bidentate nitrate ions in the coordination sphere. The nitrates again are approximately *trans* to one another with a N–Cd–N angle of 140°, but they are much more planar with a dihedral angle of 15.8(6)°. The three Schiff base oxygen donors form a highly distorted arrangement about Cd, in fact it is nearly T-shaped with O–Cd–O *cis* angles of 86–110° and a *trans* angle of 164° (see Table 2). Again there are significant changes in the arm-ring dihedral angles relative to that in the free ligand (56.3(2)°). The C(1)–C(5) arm and the C(12)–C(16) arm make dihedral angles of 39.5(3)° and 33.7(3)° with the C(6)–C(11) ring, respectively; the C(17)–C(21) arm makes a dihedral angle of 36.0(8)° to the ring defined by C(22)–C(24). Sections of three consecutive ligand strands run parallel to one another. The phenyl rings in these consecutive strands are eclipsed, with the two outer rings parallel (due to the inversion center in the central ring); the central ring is turned 29.1(8)° with respect to the outer rings.

As mentioned in Section 1, Cd was chosen as the metal center with the hope of studying the complexes by NMR if X-ray quality crystals were not forthcoming. Lack of sufficient solubility, even in EtOH from which crystals were grown, precluded these NMR experiments. IR spectroscopy is not helpful in elucidating the structure of these complexes. The N–H and C–H regions remain extremely weak and broad as described above for the free ligands, the carbonyl stretch remains weak with no significant shift, and there is a decrease of about 20 cm^{-1} in the C–C ring stretching mode. Although there is considerable overlap with ligand bands, knowing that there is bidentate nitrate coordination allows assignment of a band about 1450 cm^{-1} to ν(N=O) and a band about 1290 cm^{-1} to ν_a(NO$_2$).

3.3. Conclusions

We have shown that Schiff base ligands **L1** and **L2** can be made to coordinate to Cd(II) without deprotonation. The resulting structures **I** and **II** do not have the expected [Cd(L)(NO$_3$)$_2$] stoichiometry, but instead [Cd(**L1**)$_2$(NO$_3$)$_2$] and [Cd$_2$(**L2**)$_3$(NO$_3$)$_4$], respectively. The structures of the complexes are polymeric, involving eight-coordinate Cd in one case and seven-coordinate Cd in the other. In both cases, the ligands function as bridging bidentate keto-amine tautomers in which the NH$\cdots$O hydrogen bonding networks present in the free ligands are preserved. In **I** neighboring Cd atoms are connected by pairs of ligands, forming a double-strand chain structure, while in **II** neighboring Cd atoms are connected by single ligands, forming a single-strand chain structure.

While one cannot extrapolate the structures found for the two cadmium complexes to all of the compounds containing neutral tetradentate Schiff bases listed in Section 1, our results suggest that the structures of these latter compounds might be more complicated than originally thought. It does seem that the dimeric structures proposed by Aggarwal and Narayana [21] for **L1** and **L2** complexes of cobalt, copper, and zinc are probably not possible due to steric constraints imposed

by the ligands. It is more likely that they have polymeric structures similar to those seen here. It is interesting that the structures of **I** and **II** are quite similar to that proposed for $Re_2O_2Cl_6(PPh_3)_2(H_2SB)$ [15]. In the latter case there is only one coordination position available on each Re to which the ligand can attach, so the proposed dimeric structure seems quite reasonable and consistent with our results. It would be of great interest to examine the structures of the previously reported uranyl complexes [16,17], especially those containing coordinated sulfate and nitrate where insufficient and/or sterically hindered coordination sites are likely.

4. Supplementary material

CCDC 209324–209327 contain the supplementary crystallographic data for **L1**, **L2**, **I**, and **II**, respectively. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Director, Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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