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Article

Blue Dimetallic Complexes of Two Heavy Metal Ions Cd^{II} and Hg^{II} with an Extended Nitrogen Donor Ligand. Preparation, Spectral Characterization, and Crystallographic Studies

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In methanol, the metal salts $CdCl_2 \cdot H_2O$ and $HgCl_2$ react instantaneously with the deprotonated ligand, L^-, producing molecular dimetallic ink-blue complexes of general formula $M_2Cl_2L_2$, M = Cd(II), (**1**) and Hg(II), (**2**) (HL = 2-[2-(pyridylamino)phenylazo]pyridine). Crystal structures of these two complexes are reported. The coordination sphere around each Cd(II) ion in **1** is a distorted square pyramidal. The metal ion (Cd1) sits above the basal plane of three nitrogen atoms, N(1), N(3), and N(4). The second cadmium ion (Cd2) in this compound lies below the plane of three nitrogen atoms, N(6), N(8), and N(9). The apical positions are occupied by two Cl atoms. Secondary intramolecular interactions between the metal ions and the anionic secondary amine nitrogen atoms (N(4) and N(9)) are noted. The geometry of each Hg(II) ion in the mercury complex, $Hg_2Cl_2L_2 \cdot 0.5H_2O$, is also distorted square based pyramid with the metal ions lying out of planes of the three nitrogen atoms of the chelating ligands. Secondary Hg(1)···N(1A) (deprotonated amine) interactions are noted. The separation between the two Hg(II) ions in this complex is within the sum of their van der Waals radii. Solution properties of these blue complexes are reported. The origin of the intense blue color in these complexes is the intraligand transitions that occur near 615 nm. ^1H NMR of $Hg_2Cl_2L_2 \cdot 0.5H_2O$ indicates that it undergoes exchange in solution with the coordinated ligands.

Introduction

This work stems from our interest in d^{10}-metal complexes that absorb[1] in the low energy part of the visible region. In this respect, we recently have reported two ink-blue complexes of In(III) and Zn(II) of a nitrogenous polydentate ligand, HL (HL = 2-[2-(pyridylamino)phenylazo]pyridine), or its conjugate base, L^-. While the indium complex [$InCl_3$-HL] is monometallic and zwitterionic, the zinc complex [$Zn_2Cl_2L_2$], on the other hand, is dimetallic.[2] Such results have encouraged us to investigate the coordination of this ligand to the two heavy d^{10}-metal ions, viz. Cd^{II} and Hg^{II}. The coordination chemistry of these two metal ions has been the focus of recent attention largely due to their inherent toxic effects on the living organism.[3] There have been continuous efforts in the design and development of suitable ligands (complexing agents) for their detection as well as extraction from the source.[4] Since most of the d^{10}-metal complexes resemble the color of the coordinated ligands, fluorometric techniques have generally been used for the assessment of metal−ligand binding.[1a,3d] In comparison, however, examples of visible color change, due to complexation[1b] in these systems, are rare in the literature.

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(1) (a) Crosby, G. A.; Highland, R. G.; Truesdell, K. A. *Coord. Chem. Rev.* **1985**, *64*, 41. (b) Ibrahim, R.; Tsuchiya, S.; Ogawa, S. *J. Am. Chem. Soc.* **2000**, *122*, 12174.

(2) Das, S.; Hung, C.-H.; Goswami, S. *Inorg. Chem.* **2003**, *42*, 5153.

(3) (a) Cotton, F. A.; Wilkinson, G.; Murillo, A. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley and Sons: New York, 1999; p 598. (b) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 5, Chapter 56.1, p 925. (c) Brodersen, K.; Hummel, H.-U. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 5, Chapter 56.2, p 1047. (d) Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Isaia, F.; Garau, A.; Lippolis, V.; Jalali, F.; Papke, U.; Shamsipur, M.; Tei, L.; Yari, A.; Verani, G. *Inorg. Chem.* **2002**, *41*, 6623 and references therein. (e) Dakanali, M.; Kefalas, E. T.; Raptopoulou, C. P.; Terzis, A.; Mavromoustakos, T.; Salifoglou, A. *Inorg. Chem.* **2003**, *42*, 2531.

(4) Yordanov, A. T.; Roundhill, D. M. *Coord. Chem. Rev.* **1998**, *170*, 93.

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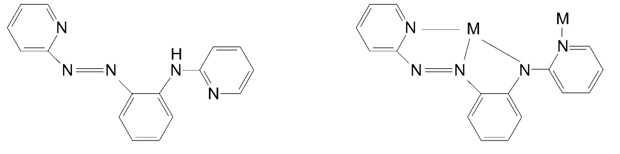
Scheme 1



HL

Bridging di-metallic coordination of L^-

In this paper, we report two blue dimetallic Cd_2- and Hg_2-complexes of the orange anionic ligand, L^-. Beside their toxological and environmental importance, these metal ions also show structural peculiarities[3a,b] in their complexes due to the tolerance for different coordination numbers and geometries. Metallophilic Hg(II)···Hg(II) attraction in di- and polymetallic systems has been studied in recent years.[5] To assess the influence of the large mercury(II) cation in the dimetallic ligand framework, the X-ray structure of the dimercury complex is compared with those of dizinc and dicadmium compounds in identical ligand environments. It may be relevant to add that, apart from halide and chalcogenide bridges,[6] some examples of dimercury complex are also available[7] in the literature.

Results and Discussion

The Ligand and the Synthetic Reaction. The ligand (HL), used in this work, was recently designed and synthesized in our laboratory by regioselective fusion of the 2-aminopyridyl function to coordinated 2-(phenylazo)pyridine.[8] Its conjugate base (L^-) acts as a potential bridging ligand. In the recent past, a few dimetallic complexes of nickel(II), palladium(II), and zinc(II) have been noted[2,8] by us (Scheme 1).

The metal salts MCl_2 (M = Cd and Hg) react almost instantaneously with an equimolar quantity of deprotonated HL in methanol resulting in dimetallic complexes of formula $M_2Cl_2L_2$ in good yields (50−60%). There were distinct color changes from orange (free L^-) to ink-blue ($M_2Cl_2L_2$) in both cases.

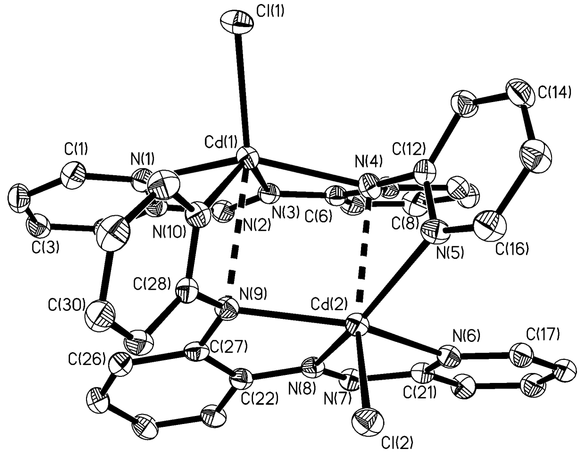


Figure 1. ORTEP and atom numbering scheme for $[Cd_2Cl_2L_2]$, **1**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) for $[Cd_2Cl_2L_2]$, **1**, and $[Hg_2Cl_2L_2\cdot 0.5H_2O]$, **2**

1		**2**	
Cd(1)−N(1)	2.371(2)	Hg(1)−N(4)	2.516(4)
Cd(1)−N(3)	2.3561(19)	Hg(1)−N(2)	2.398(3)
Cd(1)−N(4)	2.3139(18)	Hg(1)−N(1)	2.312(4)
Cd(1)−N(10)	2.2801(18)	Hg(1)−N(5A)	2.306(3)
Cd(1)−Cl(1)	2.4567(6)	Hg(1)···Hg(1A)	3.4981(4)
Cd(2)−N(6)	2.4053(18)	Hg(1)−Cl(1)	2.4951(10)
Cd(2)−N(8)	2.3507(19)	N(2)−N(3)	1.276(4)
Cd(2)−N(9)	2.3413(18)	C(11)−N(2)	1.388(5)
Cd(2)−N(5)	2.304(2)	C(12)−N(3)	1.418(5)
Cd(2)−Cl(2)	2.4569(6)	C(5)−N(1)	1.381(5)
N(2)−N(3)	1.269(3)	C(6)−N(1)	1.367(4)
C(5)−N(2)	1.422(3)		
C(6)−N(3)	1.384(3)		
C(11)-N(4)	1.367(3)		
C(12)-N(4)	1.398(3)		
N(7)−N(8)	1.274(3)		
C(21)−N(7)	1.417(3)		
C(22)−N(8)	1.385(3)		
C(27)−N(9)	1.358(3)		
C(28)−N(9)	1.385(3)		

X-ray Structures. (a) $Cd_2Cl_2L_2$ (1). The X-ray structure of the dicadmium complex is shown in Figure 1, and its bond parameters are collected in Table 1. Each cadmium atom in this molecule is in a pentacoordinate N_4Cl environment. The three nitrogen atoms viz. N(1), N(3), and deprotonated N(4) of one L^- bind to Cd(1) as a bis-chelating tridentate ligand while the second pyridyl nitrogen N(5) bridges to another Cd(2) atom. Tridentate coordination of one L^-, and a pyridyl nitrogen coordination of a second L^- ligand, together with one chloride, thus completes five-coordination about each cadmium. Because of constraints of the ligand, the geometry around each cadmium atom deviates from both square pyramidal or trigonal bipyramidal structure. To have an idea about the degree of distortion about each metal atom, we performed calculations based on the methods[9] of Addison et al. The geometric parameter, τ, for Cd(1) is 0.02, and that for Cd(2) is 0.16. The values indeed indicate[9,10] that the geometry around the metal atom is closer to a regular square based pyramid. The three coordinating nitrogen atoms, N(1), N(3), and N(4), form a good plane, and Cd(1) sits above

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(5) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (b) Pyykkö, P.; Straka, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489. (c) King, J. B.; Haneline, M. R.; Tsunoda, M.; Gabbai, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 9350. (d) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225.

(6) (a) Vezzosi, I. M. *Polyhedron* **1993**, *12*, 2235. (b) Govindaswamy, N.; Moy, J.; Millar, M.; Koch, S. A. *Inorg. Chem.* **1992**, *31*, 5343. (c) Lopez-Garzon, R.; Godino-Salido, M. L.; Gutierrez-Valero, M. D.; Arranz-Mascaros, P.; Moreno, J. M. *Inorg. Chim. Acta* **1996**, *247*, 203. (d) Mugesh, G.; Singh, H. B.; Patel, R. P.; Butcher, R. J. *Inorg. Chem.* **1998**, *37*, 2663.

(7) (a) Callot, H. J.; Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7729. (b) Spek, A. L.; Siedle, A. R.; Reedijk, J. *Inorg. Chim. Acta* **1985**, *100*, L15. (c) Mauro, A. E.; Pulcinelli, S. H.; Santos, R. H. A.; Gambardella, M. T. P. *Polyhedron* **1992**, *11*, 799. (d) Dewan, J. C.; Kepert, D. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 490. (e) Elder, R. C.; Halpern, J.; Pond, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 6877. (f) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907. (g) García-España, E.; Latorre, J.; Luis, S. V.; Miravet, J. F.; Pozuelo, P. E.; Ramírez, J. A.; Soriano, C. *Inorg. Chem.* **1996**, *35*, 4591. (h) Lye, P. G.; Lawrance, G. A.; Maeder, M.; Skelton, B. W.; Wen, H.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1994**, 793.

(8) Kamar, K. K.; Das, S.; Hung, C.-H.; Castiñeiras, A.; Rillo, C.; Kuzmin, M.; Goswami, S. *Inorg. Chem.* **2003**, *42*, 5367.

(9) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

this plane by 0.3537(23) Å. The second metal ion, Cd(2), lies below the plane formed by three coordinated nitrogen atoms, N(6), N(8), and N(9), by 0.2742(23) Å. The direction of displacement of the two cadmium atoms from the respective plane is opposite. The separation between the two Cd atoms is 3.6172(3) Å, which indicates no interaction between the two cadmium centers. The cadmium−nitrogen bond lengths [e.g., Cd(1)−N(1), 2.371(2) Å; Cd(1)−N(3), 2.3561(19) Å; Cd(1)−N(4), 2.3139(18) Å; Cd(1)−N(10), 2.2801(18) Å] all are appreciably smaller than the upper limit for the covalent Cd−N distance, 2.54(1) Å. Similar Cd−N bond lengths have been noted before in the cadmium complexes of porphyrines and other nitrogenous ligands.[11] The two Cd−Cl lengths in it are similar (mean, 2.4568(6) Å) and are comparable to the reported [11c] Cd−Cl bonds in cadmium−chloro complexes. There also exist two longer Cd···N contacts [Cd(1)−N(9), 2.7599(18) Å and Cd(2)−N(4), 2.664(2)Å] in this compound, which are longer than a typical covalent Cd−N length but are shorter[12] than the sum of van der Waals radii of Cd and N (3.15 Å). This kind of contact between Cd and N may be ascribed as a secondary intramolecular interaction. These sort of weak interactions (Cd···N) were noted before in other cadmium complexes.[11a,c] The ability of the deprotonated secondary amine function of L^- to interact simultaneously with two metal ions, with one short and one long Ni−N (amide) bond, has been noted before[8] in a dinickel complex, $Ni_2Cl_2L_2$. A similar trend is observed in the present dicadmium complex.

(b) $Hg_2Cl_2L_2 \cdot 0.5H_2O$ (2). A literature survey has revealed[3a,3c] that dimercury(II) systems with extended multidentate ligands are rare. However, structure analysis of such systems is important in the context of deriving evidence in favor of Hg(II)···Hg(II) metallophilic attraction.[5] The molecular complex, $Hg_2Cl_2L_2 \cdot 0.5H_2O$, is located at the crystallographic two-fold axis; only half of it occupies the asymmetric unit. Figure 2 shows the ORTEP and atom numbering scheme. The geometry around each Hg(II) ion may be best described as distorted square pyramidal with τ equal[9,13] to 0.06. Its bond parameters are collected in Table 1. The bonding pattern of the two anionic ligands in **2** is similar to that in its dicadmium analogue. The four Hg−N lengths [Hg(1)−N(1), 2.312(4) Å; Hg(1)−N(2), 2.398(3) Å; Hg(1)−N(4), 2.516(4) Å; and Hg(1)−N(5A), 2.306(3) Å] are well below the upper limit of a typical Hg−N covalent bond (2.75(2) Å).[14] Hg(1) lies out of the plane of three coordinating nitrogen atoms viz. N(1), N(2), and N(4) by 0.1246(42) Å. This is similar to the structures[2,15] of other two related $M_2Cl_2L_2$ [M = Zn(II) and Cd(II)] complexes, where the metal ions lie above and below the two planes. The separation between the two mercury atoms is 3.4981(4) Å, which is similar to the sum[5] of van der Waals radii of two Hg(II), 3.50(7) Å. Hence, a metallophilic Hg(II)···Hg(II) interaction in this compound may be anticipated. The Hg−Cl bond (2.4951(10) Å) is a little longer[14a,7a] than those observed in the reported mercury(II) complexes. Notably, the separation between Hg(1)···N(1A) is 2.934(4) Å, which signifies a poor intramolecular secondary interactions.[14a,16] Divalent mercury often displays linear two coordination or tetrahedral four coordination in its complexes. However, higher coordination number (>4) complexes of Hg(II) in which all the donor nitrogen atoms are the part of chelating organic ligands are uncommon.[7c,17] The Hg_2-molecule contains 0.5 water as solvate. The packing diagram showed that the water is trapped between the two chlorides of the dimer. It also showed layer structure in the crystal lattice with close contacts within the layer.

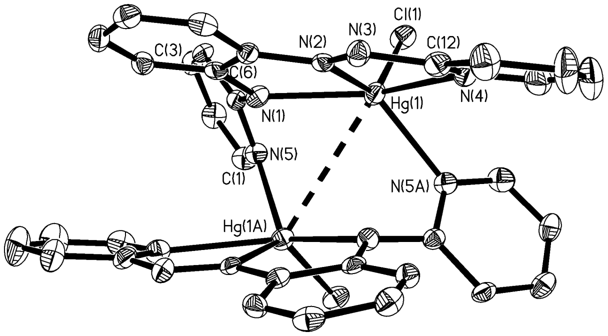

Figure 2. ORTEP and atom numbering scheme for $[Hg_2Cl_2L_2 \cdot 0.5H_2O]$, **2**. Hydrogen atoms are omitted and symmetry generated atoms are not labeled for clarity.

Spectra. Infrared spectra (Table 2) of $M_2Cl_2L_2$ [M = Cd(II) and Hg(II)] complexes are mostly similar with $\nu_{N=N}$ and ν_{M-Cl} appearing in the ranges 1305−1325 cm^{-1} and 270−280 cm^{-1}, respectively.

Both the complexes are freely soluble in nonpolar solvents such as CH_2Cl_2 and $CHCl_3$ and produce ink-blue solutions. Their UV−vis spectra are similar with lowest energy

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(10) The "geometric parameter" τ is defined[9] as $\tau = (\beta - \alpha)/60$, where β is the largest and α is the second largest of the $L_{basal}-M-L_{basal}$ angles. In the present case, the apical atoms are Cl(1) and Cl(2) while the basal atoms are N(1), N(3), N(4), N(10) for Cd(1) and N(5), N(6), N(8), N(9) for Cd(2). The β angle [N(3)−Cd(1)−N(10)] for Cd(1) is 135.88(6)°, and the α angle [N(1)−Cd(1)−N(4)] is 134.88(7)°. Similarly for Cd(2), these two angles are 144.45(6)° and 134.77(6)°, respectively.

(11) (a) Yang, F.-A.; Chen, J.-H.; Hsieh, H.-Y.; Elango, S.; Hwang, L.-P. *Inorg. Chem.* **2003**, *42*, 4603. (b) Sessler, J. L.; Murai, T.; Lynch, V. *Inorg. Chem.* **1989**, *28*, 1333. (c) Fondo, M.; Sousa, A.; Bermejo, M. R.; Garcia-Deibe, A.; Sousa-Pedrares, A.; Hoyos, O. L.; Helliwell, M. *Eur. J. Inorg. Chem.* **2002**, 703.

(12) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins College: New York, 1993; pp 114, 292.

(13) In this structure, the nitrogen atom N(5A) is apical. The angles,[9] α angle [N(1)−Hg(1)−N(4)]and β angle [N(2)−Hg(1)−Cl(1)], respectively, are 134.09(10)° and 137.56(7)°.

(14) (a) Wang, M.-C.; Sue, L.-S.; Liau, B.-C.; Ko, B.-T.; Elango, S.; Chen, J.-H. *Inorg. Chem.* **2001**, *40*, 6064. (b) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E.; Hayhurst, G. *Inorg. Chem.* **1981**, *20*, 2414. (c) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E. *Inorg. Chem.* **1981**, *20*, 4293.

(15) Due to the crystallographic imposed symmetry, the two Hg atoms in **2** are above and below the respective planes. It is also to be noted that the Zn atom is not coplanar[2] with the plane of three nitrogen atoms, viz. N(1), N(3), and N(4), but actually lies above the plane by 0.1069 Å.

(16) (a) Casas, J. S.; Castellano, E. E.; Garcia-Tasende, M. S.; Sanchez, A.; Sordo, J.; Vazquez-Lopez, E. M.; Zuckerman-Schpector, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1973. (b) Atwood, J. L.; Berry, D. E.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1983**, *22*, 3480.

(17) (a) Bebout, D. C.; Ehmann, D. E.; Trinidad, J. C.; Crahan, K. K.; Kastner, M. E.; Parrish, D. A. *Inorg. Chem.* **1997**, *36*, 4257. (b) Bebout, D. C.; Garland, M. M.; Murphy, G. S.; Bowers, E. V.; Abelt, C. J.; Butcher, R. J. *J. Chem. Soc., Dalton Trans.* **2003**, 2578 and references therein.

Table 2. Spectral Data

		chemical shift[c,d] in ppm			IR (KBr) (ν,cm^{-1})		
compd	abs[a] [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]	N−H	pyridyl proton	aromatic proton	ν(C=N)	ν(N=N)	ν_t(M−Cl)
HL	450 (5300), 315 (14550) 275 (19000)	10.21(s)	8.74 (d), 7.93 (t) 7.64 (t), 8.28(d) 8.00 (d), 7.48 (t) 7.51 (t), 8.68(d)	7.84 (d), 6.90 (t) 7.05(t), 7.02 (d)	1595	1450	
L^{-b}	455 (5425), 315 (12300) 280 (17200)						
$[H_2L]ClO_4$	450 (5300), 315 (13300) 270 (19800), 215 (55550)	10.44 (s)	8.72 (d), 7.93 (t) 7.65 (t), 8.01 (d) 8.11 (d), 7.58 (t) 7.64 (t), 8.13 (d)	7.82 (d), 7.03 (t) 7.34 (t), 7.30 (d)	1590	1450	
1	610 (7550), 470^e (2300) 350 (23100), 315^e (20625) 255 (28060), 230 (28930)		8.52 (d), 7.78 (t) 7.51 (d), 7.48 (d) 7.26 (t), 7.20 (t)	7.33 (d), 6.44 (t) 6.22 (t), 5.82 (d)	1590	1325	270
2[f]	615 (6260), 475^e (3700) 330^e (19380), 280 (26575) 230 (26500)		8.68 (d), 7.83 (t) 7.49 (d), 7.40 (d) 7.23 (t), 7.11 (t)	7.32 (d), 6.33 (t) 6.22 (t), 5.58(d)	1580	1305	280

[a] Solvent: acetonitrile for L^- and $[H_2L]ClO_4$; dichloromethane for HL, **1**, and **2**. [b] The conjugate base, L^-, was generated in situ by the addition of NEt_3 to a solution of HL in acetonitrile. [c] Solvent: DMSO-d_6 for $[H_2L]ClO_4$ and $CHCl_3$-*d* for the rest. [d] Multiplicity (s = singlet, d = doublet, t = triplet). [e] Shoulder. [f] NMR was recorded at 218 K.

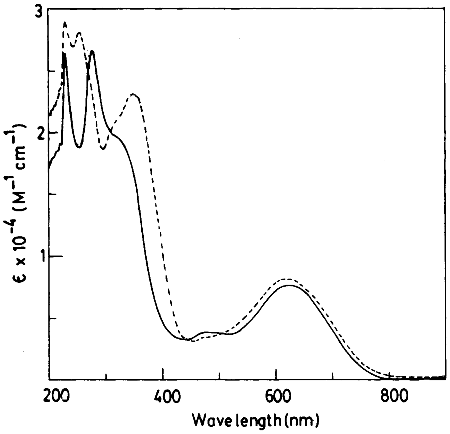

Figure 3. UV−vis spectra of **1** (- - -) and **2** (—) in dichlomethane.

transitions near 615 nm, which is associated with a shoulder/peak in the range 470−490 nm. (Table 2). In addition, there are multiple transitions in the UV region. The spectra of $Cd_2Cl_2L_2$ and $Hg_2Cl_2L_2{\cdot}0.5H_2O$ are displayed in Figure 3. The lowest energy transition in [L^-] (450 nm) is red-shifted considerably to ca. 615 nm in its complexes. Notably, the color of all the complexes of [L^-] involving d^{10}-metal ions are ink-blue, while the colors of its transition metal complexes were different.[8] In all the d^{10}-metal complexes, the levels that are involved in transitions are ligand orbitals. Modification of the properties of ligand orbitals in the present systems is due to increased planarity in the ligand frame.[1b,2] Such intensely colored d^{10}-metal complexes are rare in the literature. This ligand system thus may be useful for the detection and extraction of the toxic metal ions such as Cd(II) and Hg(II).

In the ^1H NMR spectrum in $CDCl_3$ at 298 K of the dicadmium complex, all 12 resonances of coordinated L^- were visible (Figure 4a). The absence of NH resonance in the spectrum confirms the presence of the conjugate base, L^-, in the complex. The spectrum indicates that the two ligands are magnetically equivalent. The four phenyl protons resonated in the region 7.35−5.50 ppm, while the eight pyridyl resonances were observable in the range 8.75−7.00 ppm. In contrast, the room temperature (298 K) ^1H NMR spectrum of the mercury analogue, $Hg_2Cl_2L_2{\cdot}0.5H_2O$, showed a broad spectrum; the phenyl proton resonances were particularly broad. However, the spectrum became relatively sharp at subnormal temperatures (<250 K). Two representative spectra of **2** at 298 K and at 218 K are shown in Figure 4b,c, respectively. The broad nature of ^1H NMR spectra of Hg(II)-complexes are attributed to their inherent nature of undergoing rapid exchange in solution with the coordinated ligands.[17] With decrease of temperature, the exchange process becomes slow, and hence, a sharp spectrum is observed at a low temperature.

Conclusion

X-ray structures and studies of their solution properties of two dimetallic complexes of Cd(II) and Hg(II) of an extended nitrogenous ligand, HL, are the two primary concerns of this report. These two metal ions form ink-blue complexes. Di- and polymetallic cadmium and mercury complexes are mostly obtained using a chalcogenide as the bridging ligand. However, such examples using extended nitrogen atom containing bridges are rare. Moreover, the work described herein provides an opportunity to compare and contrast the chemistry of all three group-12 metal ions with the polydentate nitrogen donor, L^-. Interestingly, the two Hg(II) ions in $Hg_2Cl_2L_2{\cdot}0.5H_2O$ are held within the sum of their van der Waals radii, and thus, it may turn out to be one of the rare examples suitable for the study of metallophilic attractions in closed shell Hg(II) systems.

Experimental Section

A JASCO V-570 spectrometer was used to record electronic spectra. The IR spectrum (4000−400 cm^{-1}) and far-IR spectrum (400−50 cm^{-1}) were recorded using Magna-IR 750 series-II and FTIR Bomen DA 8.3 spectrometers, respectively. ^1H NMR spectra were recorded on a Bruker Avance DPX 300 using TMS as the internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N).

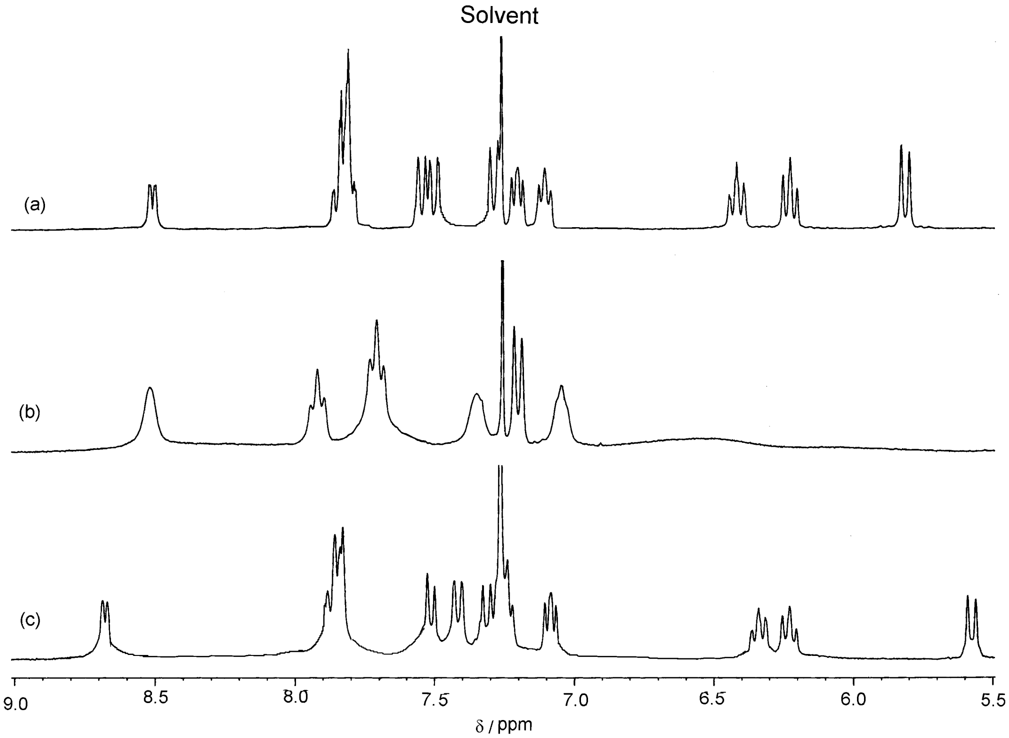

Figure 4. ^1H NMR spectra of (a) **1** at 298 K, (b) **2** at 298 K, and (c) **2** at 218 K in $CDCl_3$.

Solvents and chemicals used for synthesis were of analytical grade. The ligand HL is prepared following the procedure reported previously.[8]

Synthesis of Compounds. $[Cd_2Cl_2L_2]$. The ligand HL (100 mg, 0.363 mmol) was dissolved in 25 mL of methanol, and 1−2 drops of triethylamine was added. To this deprotonated ligand solution was added an aqueous solution of $CdCl_2\cdot H_2O$ (75 mg, (0.372 mmol, in 2 mL of water), and the mixture was stirred for 30 min at room temperature. The color of the solution immediately changed from orange to deep blue, and a dark compound was precipitated. The precipite was collected by filtration. It was then washed thoroughly with diethyl ether and air-dried in a vacuum descicator. The crude product was then recrystallized from a chloroform−acetonitrile solvent mixture. Yield: 50%. Anal. Calcd for $C_{32}H_{24}N_{10}Cl_2Cd_2$: C, 45.48; H, 2.84; N, 16.58. Found: C, 45.51; H, 2.88; N,16.62.

$[Hg_2Cl_2L_2\cdot 0.5H_20]$. This was prepared similarly by reacting an appropriate quantity of $HgCl_2$ (100 mg, (0.368 mmol, in 2 mL of water) (in place of $CdCl_2\cdot H_2O$) with the deprotonated ligand $[L^-]$ as described above. Crystals were grown by diffusion of toluene into a dichlomethane solution of the compound. Yield: 60%. Anal. Calcd for $C_{32}H_{24}N_{10}Cl_2Hg_2\cdot 0.5H_2O$: C, 37.29; H, 2.42; N, 13.59. Found: C, 37.32; H, 2.44; N,13.62.

X-ray Structure Determination. The crystal data of $[Cd_2Cl_2L_2]$, **1**, and $[Hg_2Cl_2L_2\cdot 0.5H_2O]$, **2**, are collected in Table 3.

$[Cd_2Cl_2L_2]$. The X-ray quality crystals of $[Cd_2Cl_2L_2]$ were obtained by slow diffusion of acetonitrile into a chloroform solution of the compound. The data were collected on a Bruker SMART diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å), and data were corrected for Lorentz-polarization effects. A total of 20314 reflections were collected out of which 7456 were unique ($R_{int} = 0.0239$) and were used in subsequent analysis. The SADABS absorption corrections were applied.[18] The structure was solved by employing the SHELXS 97 program package[19] and refined by full-matrix least-squares based on F^2.

Table 3. Crystallographic Data for the Compounds $[Cd_2Cl_2L_2]$, **1**, and $[Hg_2Cl_2L_2\cdot 0.5H_2O]$, **2**

	$[Cd_2Cl_2L_2]$	$[Hg_2Cl_2L_2\cdot 0.5H_2O]$
empirical formula	$C_{32}H_{24}N_{10}Cl_2Cd_2$	$C_{32}H_{25}N_{10}Cl_2O_{0.5}Hg_2$
molecular mass	844.31	1029.7
temp [K]	100(2)	100(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a [Å]	11.6626(7)	12.2518(7)
b [Å]	14.5023(8)	17.6724(11)
c [Å]	19.3361(11)	14.6974(9)
α [deg]	90	90
β [deg]	93.0910(10)	90.6520(10)
γ [deg]	90	90
V [Å^3]	3265.6(3)	3182.1(3)
Z	4	4
D_{calcd} [Mg/m^3]	1.717	2.149
cryst dimens [mm^3]	0.56 × 0.28 × 0.18	0.43 × 0.20 × 0.12
θ range for data collection [deg]	1.75−27.52	2.02−27.47
wavelengths [Å]	0.71073	0.71073
reflns collected	20314	9950
unique reflns	7456	3625
abs correction	empirical used SADABS	empirical used SADABS
max and min transm	0.9486 and 0.6974	0.9486 and 0.7066
largest diff. between peak and hole [e Å^{-3}]	0.866, −0.622	1.546, −1.549
final R indices [$I > 2\sigma(I)$]	R1 = 0.0231 wR2 = 0.0595	R1 = 0.0245 wR2 = 0.0317

$[Hg_2Cl_2L_2\cdot 0.5H_20]$. The X-ray quality crystals of $[Hg_2Cl_2L_2\cdot 0.5H_2O]$ were obtained by slow diffusion of toluene into dichloromethane solution of the compound. The data were collected as noted above. A total of 9950 reflections were collected out of which 3625 were unique ($R_{int} = 0.0401$) and were used in subsequent analysis. The SADABS absorption corrections were applied.[18] The

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(18) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction Program;* University of Göttingen: Göttingen, Germany, 1996.

(19) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL, 97, Program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

structure was solved by employing the SHELXS 97 program package[19] and refined by full-matrix least-squares based on F^2.

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Supporting Information Available: X-ray crystallographic details of the two compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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