*J. Chem. Research (S)*, 1999, 494–495†

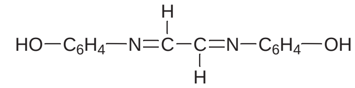
# Preparation and Characterization of Complexes formed by the Reaction of Bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-diene with Zinc, Cadmium and Mercury Chlorides†

**Morteza F. Farnia, Mansour Abedini* and Mohammad Ali Pazukian**

*Department of Chemistry, Tehran University, Tehran, 14155-6455, Iran*

Complexes of bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-diene with $Zn^{II}$, $Cd^{II}$ and $Hg^{II}$ chlorides are synthesized; the complexes of $Zn^{II}$ and $Cd^{II}$ are mononuclear with the ligand as a chelate, whereas the $Hg^{II}$ complex is dinuclear with the ligand bridging two Hg nuclei.

The ligand used in this work **1** is an α- or 1,2-diimine and is formed by condensation of one mole of glyoxal with two moles of *p*-aminophenol. Its structure is as follows:



$$HO{-}C_6H_4{-}N{=}\overset{\overset{H}{|}}{C}{-}\underset{\underset{H}{|}}{C}{=}N{-}C_6H_4{-}OH$$

**1**

The above arrangement, *E-s-trans-E*, is the most stable one in both solution and in the solid state.[1–3] Since α-diimines could be regarded as derivatives of 1,4-diazabuta-1,3-diene, in most references they are indicated as R-DAB{R′,R″} where R is the substituent group on imine nitrogens and R′ and R″ are substituent groups on imine carbons. Complexes of these types of ligands with different metal ions and their properties have been reviewed.[4,5] Coordination of R-DAB to metal ions takes place in different modes, as monodentate (σ-N),[6] 4e bridge (σ-N, σ-N′)[7,8] 6e bridge (σ-N, $\mu^2$-N′, $\eta^2$-C=N′),[9] 8e bridge (σ-N, σ-N′, $\eta^2$-C=N, $\eta^2$-C=N′)[10–12] and finally as a chelate (σ, σ, *N*, *N*′).[13,14] The latter is the most common mode of coordination for this ligand. Most complexes that have been studied with metal ions in their normal oxidation states have alkyl substituents on their imine nitrogens. The purpose of the present work was to choose a diimine ligand with aryl groups on the imine nitrogens, and to find its preferential mode of coordination to the group 12 metal ions. Although these ions have a $d^{10}$ configuration and there is no d–d electronic transition in these complexes, the ligand itself has a chromophore group that strongly absorbs in the ultraviolet region. However, since the pattern and intensity of the absorption bands change upon complexation of the ligand, these changes could be used for the identification of these complexes.

## Experimental

*Materials and Instruments.*—All chemicals were obtained from Merck. The instruments used were a Shimadzu FT-IR-4300 for infrared spectra, a Brucker AC 80 for $^1$H NMR spectra and Shimadzu UV-265 FW for UV–VIS spectra.

*Preparation of Bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-diene* **1**.—This compound, which was used as a ligand, was prepared as yellow needle crystals (mp 196 °C, decomp.) by the method described in the literature.[15]

IR (Nujol, $\nu$/cm$^{-1}$): stretching vibrations; O–H 3200, C=N 1604, aromatic C=C 1573, 1502 and 1456, C–O 1240, C–N=1166; bending vibrations; O–H 1379 and 1269; out-of-plane, aromatic =C–H 833. $^1$H NMR ([$^2$H$_6$] DMSO, δ, ppm): 7.1 (q, 8H, ArH), 8.4 (s, 2H, HC=N) and 9.7 (s, 2H, ArOH). UV–VIS ($CH_2Cl_2$, $\lambda_{max}$/nm): 270 and 330.

*Preparation of Bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-dienedichlorozinc(II)*, [$ZnCl_2(C_{14}H_{12}N_2O_2)$].—Dry α-diimine as ligand (0.240 g, 1 mmol) was dissolved in 90 ml dry THF at the reflux temperature under an argon atmosphere. A solution of dry $ZnCl_2$ (0.136 g, 1 mmol) in 20 ml dry THF was added dropwise to the yellow solution of the ligand over a period of 0.5 h, the color changed from yellow to orange. Reflux was continued for another 0.5 h. The volume of this solution was halved in a rotary evaporator and it was then cooled in a refrigerator overnight. Orange needle crystals (32% yield) were recrystallized from cold acetonitrile (mp 249 °C decomp.). This compound was sensitive to moisture and its color would change to yellow upon addition of a small amount of water.

Elemental analysis: Calcd. for $ZnCl_2(C_{14}H_{12}N_2O_2)$, $M_r$, 376.5: C, 44.6; H, 3.2; N, 7.4 and Zn, 17.4%. Found: C, 44.4; H, 3.3; N, 7.1; Zn, 16.9%. Molar conductivity (MeCN, 25 °C): 2.324 S cm$^2$ mol$^{-1}$. IR (Nujol, $\nu$/cm$^{-1}$): stretching vibrations; O–H 3394; C=N, 1620 and 1581. $^1$H NMR ([$^2$H$_6$]DMSO, δ, ppm): 7.1 (q, 8H, ArH), 8.4 (s, 2H, HC=N) and 9.7 (s, 2H, ArOH). UV–VIS ($CH_2Cl_2$ $\lambda_{max}$/nm): 230 (with shoulder) and 355.

*Preparation of Diaquabis(4-hydroxyphenyl)-1,4-diazabuta-1,3-dienedichlorocadmium(II)*, [$CdCl_2(H_2O)_2(C_{14}H_{12}N_2O_2)$].—Dry α-diimine as ligand (0.240 g, 1 mmol) was dissolved in 40 ml of absolute ethanol at the reflux temperature to yield a yellow solution. $CdCl_2 \cdot 2H_2O$ (0.220 g, 1 mmol) was dissolved in 10 ml absolute ethanol and this solution was added dropwise to the solution of the ligand at the reflux temperature. The color of the solution changed to orange. Reflux was continued for 2 h and the resultant solution was held in a refrigerator overnight. The red–orange crystals obtained (76% yield) were then thoroughly washed with diethyl ether. This compound decomposed at 263 °C without melting and was sensitive to moisture, its color changed to yellow upon the addition of small amount of water and the free ligand was separated.

Elemental analysis: Calcd. for $Cd(H_2O)_2(C_{14}H_{12}N_2O_2)Cl_2$, $M_r$ 459.5: C, 36.5; H, 3.5; N, 6.1 and Cd, 24.5%; found: C, 36.4; H, 3.0; N, 5.9 and Cd, 24.1%. Molar conductivity (in $C_2H_5OH$, 25 °C): 12.48 S cm$^2$ mol$^{-1}$. IR (Nujol, $\nu$/cm$^{-1}$): stretching vibrations; O–H (water) 3467; O–H (phenolic) 3363; C=N 1618 and 1583; bending vibration, O–H (water) 1647. $^1$H NMR ([$^2$H$_6$]DMSO, δ, ppm): 7.1 (q, 8H, ArH), 8.4 (s, 2H, HC=N) and 9.7 (s, 2H, ArOH). UV–VIS ($CH_2Cl_2$, $\lambda_{max}$/nm 230 (with shoulder) and 360.

*Preparation of Bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-dienetetrachlorodimercury(II) Diethyl Ether*, [$Hg_2Cl_4(C_{14}H_{12}N_2O_2) \cdot (C_2H_5)_2O$].—Dry α-diimine ligand (0.240 g, 1 mmol) was thoroughly mixed in 10 ml diethyl ether and then a solution of $Hg^{II}$ chloride (0.271 g, 1 mmol) in 15 ml diethyl ether was gradually added to the above suspension. After a few minutes a red precipitate was formed. Mixing was continued for 1 h. This product was recrystallized from diethyl ether as red needle crystals (92% yield) (mp 189 °C; decomp.). This compound was not sensitive to moisture. However, by gentle heating, the mercury salt sublimed and the free ligand was separated as yellow crystals.

Elemental analysis: Calcd. for $Hg_2Cl_4(C_{14}H_{12}N_2O_2) \cdot (C_2H_5)_2O$, $M_r$ 857.1: C, 25.2; H, 2.6; N, 3.3; Hg, 46.8%, found: C, 25.2; H, 2.4; N, 3.4; Hg, 47.5%. Molar conductivity (in $C_6H_5NO_2$, 25 °C): 0.688 S cm$^2$ mol$^{-1}$. IR (Nujol, $\nu$/cm$^{-1}$): stretching vibrations: O–H, 3329; C=N, 1580. $^1$H NMR ([$^2$H$_6$]DMSO, δ, ppm): 7.1 (q, 8H, ArH), 8.4 (s, 2H, HC=N), 9.8 (s, 2H, ArOH). UV–VIS ($CH_2Cl_2$, $\lambda_{max}$/nm): 230, 450.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

## Results and discussion

These experiments show that bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-diene as a ligand reacts with the chlorides of $Zn^{II}$, $Cd^{II}$ and $Hg^{II}$ and that this reaction is indicated by a change of color and also a shift in particular bands in the IR spectra of the complexes formed. In the case of $Zn^{II}$ and $Cd^{II}$ ions, these complexes are formed in a 1 : 1 mole ratio, are non-electrolytes and mononuclear, with the ligand acting as a chelate. The coordination numbers of Zn and Cd in these complexes are four and six, respectively, which are compatible with their ionic radii.

However, in the case of $HgCl_2$, although a 1 : 1 mole ratio of the reactants were used, only a binuclear complex was crystallized from an ether solution and some of the ligand was left in the solution. In this case the ligand retains the stable *E-s-trans-E* arrangement and acts as a bridge between the two nuclei.

IR spectra of the above complexes were obtained in Nujol, because the ligand would dissociate from the complex at the high pressure required to make a KBr disk. The free ligand shows only one stretching vibration for the C=N group, which is consistent with the $C_{2h}$ local symmetry of the conjugated diene **1** ($B_u$ symmetry species; a $A_g$ symmetry species is IR inactive.) However, in each of the complexes of $Zn^{II}$ and $Cd^{II}$ ions there are two bands for the C=N stretching vibrations, consistent with the $C_{2v}$ local symmetry of the ligand as a chelate. In this case both $A_1$ and $B_1$ symmetry species are infrared active. In the case of the $Hg^{II}$ complex where the ligand acts as a bridge and retains its original *E-s-trans-E* configuration, again only one stretching vibration band is observed.

The $^1H$ NMR spectra of these complexes correspond exactly with the spectrum of the free ligand and are indicative of the presence of the ligand in these complexes. However, the absence of chemical shifts in these spectra, especially for the imine hydrogens, where the nitrogens of the ligand act as the ligating atoms, indicates that the coordination of ligand in these complexes is rather weak and easily displaced by the DMSO in the NMR tube. DMSO was the only high polarity solvent in which a sufficient amount of the complex could be dissolved to obtain a good $^1H$ NMR spectrum. In the $^1H$ NMR spectrum of the $Hg^{II}$ complex, peaks due to the $CH_3$ protons of diethyl ether at $\delta$ 1.07 were also observed. Peaks due to the $CH_2$ group are overlapped by the peak of the solvent.

UV–VIS spectra of these complexes were obtained in $CH_2Cl_2$, which has no coordinating ability. The two absorption bands in the spectrum of the ligand are ascribed to $\pi \rightarrow \pi^*$ (330 nm) and $n \rightarrow \pi^*$ (270 nm) transitions. In these complexes the band due to a $n \rightarrow \pi^*$ transition is shifted to a lower wavelength (230 nm) because nonbonding electrons of the ligating atoms are stabilized by coordination to the metal ions and therefore the $n$–$\pi^*$ energy gap is increased. However, the 330 nm band in the ligand is shifted to higher wavelengths [355 nm for $Zn^{II}$ 360 nm for $Cd^{II}$ and 450 nm for $Hg^{II}$] in these complexes. This shift indicates that because of the coordination of C=N groups to the metal ions, the contribution of the ionic form ($C^+-N^-$) in the resonance hybrid has increased and therefore the $\pi$ bond is weakened and its energy level is increased and shifted closer to the energy of $\pi^*$ level. This change explains the shift towards higher wavelengths. It is noted that, for the $Hg^{II}$ complex, this shift is much greater compared with the $Zn^{II}$ and $Cd^{II}$ complexes, because in the case of $Hg^{II}$ each imine nitrogen is coordinated to one $Hg^{II}$ ion whereas in other complexes both imine nitrogens are coordinated only to one metal ion. Therefore, in the $Hg^{II}$ complex, the contribution of the $C^+-N^-$ resonance form in the resonance hybrid is greater.

## Conclusions

Complexes of bis(4-hydroxyphenyl)-1,4-diazabuta-1,3-diene as a ligand with Zn, Cd and Hg chlorides have been characterized by their $^1H$ NMR, infrared and UV–VIS spectra. In the case of Zn and Cd ions the ligand acts as a chelate. However, in the case of $Hg^{II}$ the ligand retains its original *E-s-trans-E* configuration and acts as a bridge between two $Hg^{II}$ nuclei. Experimental observations indicate that the coordination of this ligand to the above metal ions is rather weak and that these complexes dissociate in solvents such as DMSO, DMF and $H_2O$. The complexes are non-electrolytes and decompose on heating.

*Received, 23rd February 1999; Accepted, 22nd April 1999*
*Paper E9/01490J*

## Reference

1 V. De Gaouk and R. J. W. Le Fevre, *J. Chem. Soc.*, 1938, 741.
2 J. M. Kliegman and R. K. Barnes, *Tetrahedron*, 1970, **26**, 2555.
3 J. Keijsper, H. van der Poel, L. H. Polm, G. van Koten and K. Vrieze, *Polyhedron*, 1983, **2**, 1111.
4 G. van Koten and K. Vrieze, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 129.
5 G. van Koten and K. Vrieze, *Adv. Organometal. Chem.*, 1982, **21**, 151.
6 L. H. Staal, D. J. Stafkens and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 255.
7 H. van der Poel, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, 1977, **135**, C63.
8 H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chim. Acta*, 1981, **51**, 241.
9 L. H. Staal, J. Keijsper, G. van Koten, K. Vrieze, J. A. Cras and W. P. Bosman, *Inorg. Chem.*, 1981, **20**, 555.
10 J. Keijsper, L. H. Polm, G. van Koten, K. Vrieze, G. Abbel and C. H. Stam, *Organometallics*, 1983, **4**, 2142.
11 J. Keijsper, L. H. Polm, G. van Koten, K. Vrieze, F. A. B. Seignette and C. H. Stam, *Inorg. Chem.*, 1985, **24**, 518.
12 L. H. Holm, G. Van Koten, C. J. Elsevier, K. Vrieze, B. F. K. van Santen and C. H. Stam, *J. Organometal. Chem.*, 1986, **304**, 353.
13 F. Geffrey, N. Cloke and H. Delemos, *J. Chem. Soc., Chem. Commun.*, 1986, 1344.
14 H. tom Dieck and I. W. Rank, *Chem. Ber.*, 1971, **104**, 92.
15 J. M. Kliegman and R. K. Barnes, *J. Org. Chem.*, 1970, **35**, 3140.