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Syntheses and Structures of Zwitterionic Indium(III) and Di-zinc Compounds of an Extended Nitrogenous Ligand. Examples of Unusually Long Wavelength Transitions in d^{10}-Metal Complexes

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In acetonitrile, the reaction of hydrated $InCl_3$ and 2-[(2-(pyridylamino)phenylazo]pyridine [HL] affords an ink-blue octahedral indium(III) complex having the formula [$InCl_3$(HL)]. The compound is a zwitterion in which the positive and the negative charges reside on the extended ligand HL. The secondary amine nitrogen in it is deprotonated, while the free pyridyl nitrogen is protonated. The reaction of $ZnCl_2$, on the other hand, produces a di-metallic complex, [$Zn_2Cl_2L_2$], where the two metal ions are bridged across the deprotonated ligand [L]$^-$. The color of the di-zinc complex is also ink blue. Interestingly, the UV–vis spectrum of the indium compound is almost identical to that of the di-zinc compound. Long-wavelength transitions near 590 nm in these examples are assigned to intraligand π–π* transitions.

Introduction

The color of metal complexes of d^{10}-metal ions originates from electronic transitions within the ligand orbitals.[1−3] Most of these are colorless, absorbing only in the UV-region. Usually the color of these complexes resembles that of the coordinated ligands.

During recent years we have been working on the binding mode of an extended polydentate ligand 2-[(2-(pyridylamino)-phenylazo]pyridine [HL]. The ligand was synthesized by oxidative fusion[4] of 2-aminopyridine to coordinated 2-(phenylazo)pyridine (pap). The ligand [HL], upon deprotonation, acts as a potential binucleating ligand for the transition metal ions.[5] We now have observed that the ligand HL when mixed with the chloride salts of In(III) and Zn(II), produce intense blue solutions. These observations prompted us to look for the compounds, which are responsible for the otherwise unusual color of the above mixtures. As far as we are aware, colored complexes of d^{10}-metal ions that absorb in the long-wavelength region are virtually unknown in the literature.[1−3,6−8] In this report we describe the isolation, X-ray structures, and solution optical properties of two blue d^{10}-metal compounds, viz., a mononuclear zwitterionic indium(III) compound and a dinuclear zinc(II) compound (Chart 1).

Results and Discussion

Indium(III) Complex. The metal salt $InCl_3{\cdot}4H_2O$ reacts instantaneously with HL to produce an ink-blue solution. There was gradual development of the color upon addition

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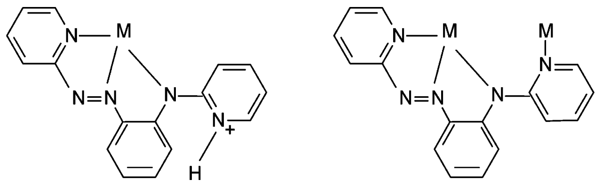
Chart 1



Cordination of the zwitterion,HL Di-metallic bridging mode of $[L]^-$

of indium(III) chloride to a solution of HL in acetonitrile. It may be noted here that the lowest energy transition of the free ligand, HL (λ_{max}, 450 nm) diminished with concomitant growth of a new transition at 594 nm (Figure 1). The absorption of this mixture became maximum for a 1:1 mixture of HL and $InCl_3{\cdot}4H_2O$. It suggests that the compound, which produces the color, is a 1:1 In−HL compound (Table 1). Monitoring the proton resonance spectrum also followed the reaction. Parts a and b of Figure 2 respectively show the spectra of free HL and the blue solution that is obtained by addition of an equimolar quantity of hydrated $InCl_3$ to HL. Notably, the broad resonance[9] due to NH (amine) in free HL (at δ 10.21) disappeared upon addition of the In(III) salt to HL and a new broad resonance at δ 8.76 appeared. This may be assigned to a pyridyl N−H resonance. The rest of the proton resonances were observed at their usual positions.

In an attempt to isolate the indium complex, a solution of HL in acetonitrile was added slowly to hydrated $InCl_3$, dissolved in a minimum of water. The mixture immediately became ink-blue from which a dark crystalline product with a bronze sheen deposited in the reaction vessel. X-ray quality crystals were chosen from the deposited material. The X-ray structure of the indium compound is shown in Figure 3. In this compound, a distorted octahedral coordination environment surrounds the indium center by three chloride ligands and a bischelating tridentate ligand, HL. The compound is a zwitterion[10] in which the positive and negative charges reside on the protonated ligand. Notably, the free pyridyl nitrogen N(5) is protonated[11] and the secondary amine nitrogen N(4) is deprotonated. The three coordinating nitrogens, viz., N(1), N(3), and N(4) along with In(1), form a good plane with no atom deviating by >0.04 Å. The Cl(2) lies out of that plane by 0.415 Å. The two chlorides, Cl(1) and Cl(3), lie trans to each other. The bond distances in this molecule suggest a high degree of delocalization in the extended ligand. The three C−N bonds, viz., C(12)−N(4) (1.357(3) Å), C(11)−N(4) (1.389(3) Å), and C(6)−N(3) (1.385(3) Å), all are appreciably shorter than the C−N single bond, C(5)−N(2) (1.431(3) Å), present in the same molecule. Moreover, the N−N length, N(2)−N(3) (1.275(2) Å), in the reference compound is longer than that for a −N═N− length observed[12] (1.258(5) Å) in a free diazo ligand, $[Hpap]ClO_4$ (pap = 2-(phenylazo)pyridine). All these taken together indeed suggest an extensive delocalization in $[InCl_3(HL)]$ along the ligand backbone of coordinated HL. It should be noted here that octahedral coordination in indium(III) is not common.[3,13] Moreover, to the best of our knowledge, the indium compound represents the first example of a zwitterionic octahedral system.

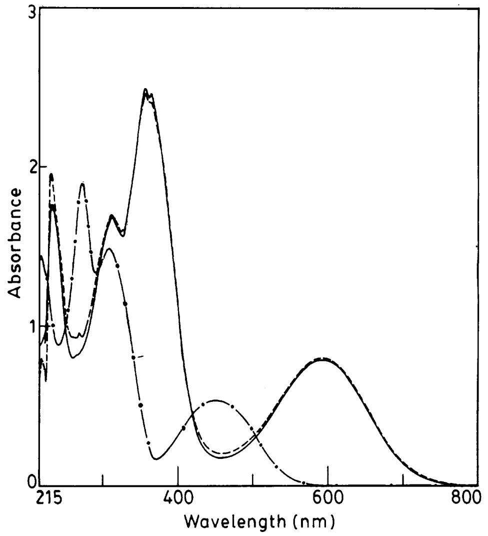


Figure 1. UV−vis spectra of $[InCl_3\ HL]$ (--) and [HL] (− • −) in acetonitrile and of $[Zn_2L_2Cl_2]$ (—) in dichloromethane.

Table 1. Optical Spectral Data

compd	abs[a] [λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)]	IR (KBr) (ν, cm^{-1}) ν(C═N)	ν(N═N)
$[InCl_3(HL)]$	594 (8020), 366 (24 350), 312 (17 050), 232 (20 100)	1590	1320
$[Zn_2Cl_2L_2]$	596 (7890), 364 (24 375), 310 (16 400), 231 (17 750)	1595	1308
[HL]	450 (5330), 312 (14 550), 275 (19 025)	1595	1450

[a] Solvent: acetonitrile for $[InCl_3HL]$ and [HL]; dichlomethane for $[Zn_2Cl_2L_2]$.

Di-zinc Complex. The reaction of $ZnCl_2$ with an equimolar quantity of HL in methanol also produced an intense blue solution. Upon slow evaporation of the reaction mixture, dark crystals of a di-zinc(II) compound of molecular formula $[Zn_2Cl_2L_2]$ was obtained in a moderate yield. The X-ray structure of this zinc complex is shown in Figure 4. Each zinc atom in this molecule is pentacoordinated and is surrounded by a N_4Cl environment. The zinc(II) ion generally is found to assume a tetrahedral geometry. However, pentacoordinated di-zinc complexes are relatively uncommon.[1,8a] The two nitrogens of the 2-(phenylazo)pyridine part (N(1) and N(3)) together with the deprotonated secondary amine nitrogen (N(4)) bind to one zinc atom as a bischelating tridentate ligand, while the second pyridyl nitrogen (N(5)) of aminopyridyl function binds to a second zinc atom. This result is in contrast to that observed in the case of indium-

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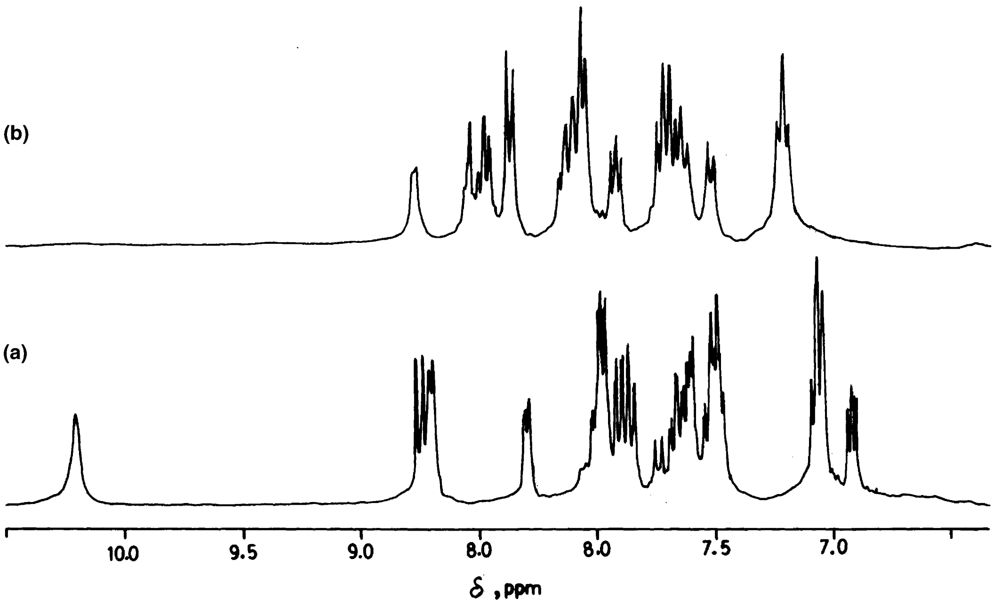

Figure 2. ^{1}H NMR spectra of (a) HL and (b) [$InCl_3HL$] in CD_3CN.

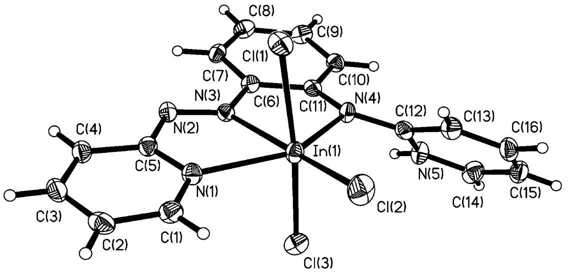

Figure 3. ORTEP diagram and atom numbering scheme for [$InCl_3HL$].

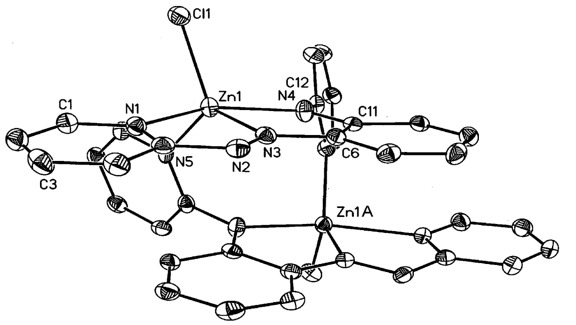

Figure 4. ORTEP diagram and atom numbering scheme for [$Zn_2L_2Cl_2$]. For clarity, symmetry generated atoms are not labeled.

(III). It is believed that lability of the starting material is crucial for the dimerization process (Scheme 1).

In the case of In(III) salt, because of its high charge, the coordinated chlorides are not labile and hence dimerization was not possible; the dangling pyridyl nitrogen (N(5)) in this case is protonated to produce a molecular, zwitterionic compound. The zinc(II) salt, on the other hand, is labile and forms a five-coordinate intermediate, which undergoes dimerization using the pendant pyridyl nitrogen to produce a pentacoordinated di-zinc complex. Our proposal of dimerization in a labile system was further strengthened by the fact that a labile Pd(II) salt when reacted with HL produced a di-palladium(II) complex while the reaction of HL with an inert Pt(IV) salt produced a monometallic platinum(IV) complex with a dangling pyridyl nitrogen.[5] Selected bond distances of the di-zinc complex are collected in Table 2. The Zn−N bond lengths lie in the range of 2.064−2.189 Å, while the Zn−Cl bond length is 2.2706(16) Å. The three coordinating nitrogens, viz., N(1), N(3), and N(4) along with Zn(1), are planar with a maxium deviation of 0.035 Å from the mean plane. The Cl(1) and the pyridyl nitrogen N(5) both lie out of that plane. The bond distances in this molecule also suggest a considerable degree of delocalization along the extended ligand backbone. As a result the N−N length (1.284(7) Å) is stretched more than a −N═N− length and the three C−N lengths, viz., C(6)−N(3) (1.385(7) Å), C(11)−N(4) (1.351(7) Å), and C(12)−N(4)(1.387(7) Å), are short compared to a C−N single bond length. These observations are similar to those observed in the indium(III) complex. Hence, in both examples there is extensive delocalization along the ligand backbone.

Scheme 1

$$ZnCl_2 + HL \longrightarrow [ZnCl_2L]^- \xrightarrow{-Cl^-} [Zn_2Cl_2L_2]$$

$$InCl_3.4H_2O + HL \longrightarrow [InCl_3HL]$$

Table 2. Selected Bond Distances (Å) and Angles (deg) for [$InCl_3HL$] and [$Zn_2Cl_2L_2$]

[$InCl_3HL$]		[$Zn_2Cl_2L_2$]	
In(1)−N(1)	2.2684(19)	Zn(1)−N(1)	2.189(4)
In(1)−N(3)	2.2577(19)	Zn(1)−N(3)	2.163(5)
In(1)−N(4)	2.2220(19)	Zn(1)−N(4)	2.095(4)
In(1)−Cl(1)	2.5775(7)	Zn(1)−N(5)	2.064(5)
In(1)−Cl(2)	2.3876(7)	Zn(1)−Cl(1)	2.2706(16)
In(1)−Cl(3)	2.4968(7)	N(2)−N(3)	1.284(7)
N(2)−N(3)	1.275(2)	C(5)−N(2)	1.402(7)
C(5)−N(2)	1.431(3)	C(6)−N(3)	1.385(7)
C(6)−N(3)	1.385(3)	C(11)−N(4)	1.351(7)
C(11)−N(4)	1.389(3)	C(12)−N(4)	1.387(7)
C(12)−N(4)	1.357(3)		
N(1)−In(1)−N(3)	69.70(7)	N(1)−Zn(1)−N(3)	70.87(17)
N(3)−In(1)−N(4)	73.76(7)	N(3)−Zn(1)−N(4)	75.60(19)
Cl(1)−In(1)−Cl(3)	170.98(2)	N(5)−Zn(1)−Cl(1)	106.26(14)

The di-zinc complex is freely soluble in nonpolar solvents such as CH_2Cl_2 and $CHCl_3$ and produces intense blue solutions.The UV−visible spectral data of the complex are collected in Table 1. The spectrum of the complex is almost identical to that of the indium compound with a strong absorption band near 590 nm, which is associated with multiple transitions in the UV region. We note here that the blue color of the coordinated ligand (HL/L^-) appears to be unique for d^{10}-metal ions. The presence of the pyridyl nitrogen is found to be essential for the formation and stabilization of the above compounds. For example, if the bridging pyridyl group is replaced by a phenyl group, no stable compound of either of the above metal ions could be isolated. Furthermore, deprotonation of [$InCl_3HL$] led to decomposition of the product. It thus indicates that interactions between the pyridyl nitrogen and a Lewis acid are also important for the formation of these blue complexes of d^{10}-metal ions.

To gain some idea of the nature of the orbitals that are responsible for long-wavelength charge transfer in the present d^{10}-metal complexes, semiemperical EHMO calculations have been performed on the above compounds and are made by making use of the CACAO program by Mealli and Proserpio.[14] The calculations were performed on the basis of atomic coordinates obtained from the X-ray crystal data analysis of the compounds. Due to obvious limitations, we note that the results presented here are only qualitative in nature. Pictorial presentations of the HOMO-1, HOMO, and LUMO of the representive compound, [$InCl_3HL$], are submitted as Supporting Information (Figure S1). All of them are ligand orbitals with negligible contribution from the metal part. These are as expected for closed shell metal complexes of the d^{10}-metal ions. Notably, while the HOMO is predominantly diazo in character, the HOMO-1 and LUMO are more delocalized with significant contributions from the diazo and the deprotonated amine part of the ligand HL (Figure S1). The lowest visible-range transitions near 590 nm in the present d^{10}-metal compounds are thus assigned to intraligand $\pi\angle\pi^*$ transitions. It may be relevant to note here that the lowest energy transition in free HL occurs at 450 nm, which shifts red appreciably upon coordination. Hence, the presence of the metal ions modify the donor−acceptor properties of the delocalized ligand orbitals to a considerable extent, possibly by imposing planarity[7] in the ligand frame.

Conclusion

An internal charge-transfer transition in the colored d^{10}-metal complexes is of interest. The d^{10}-metal complexes, which absorb in the visible range, are mostly mixed ligand systems, containing N-heterocylic and aromatic thiolato ligands. The interligand charge transfer in these occur[1] from the donor thiolato to the acceptor diimine function. In contrast, the low-energy transition in our systems occurs within the ligand framework ($\pi\angle\pi^*$). Examples of such systems are scarce in the literature. Our work in this area is continuing.

Table 3. Crystallographic Data of the Compounds [$InCl_3(HL)$] and [$Zn_2Cl_2L_2$]

	[$InCl_3(HL)$]	[$Zn_2Cl_2L_2$]
empirical formula	$C_{16}H_{13}N_5Cl_3In$	$C_{32}H_{24}N_{10}Cl_2Zn_2$
molecular mass	496.48	750.26
temp (K)	150(2)	150(2)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Fdd2$
a (Å)	10.1082(5)	29.419(2)
b (Å)	13.7005(7)	11.8121(8)
c (Å)	13.2881(7)	17.7672(13)
α (deg)	90	90
β (deg)	106.3900(10)	90
γ (deg)	90	90
V (Å)	1765.45(16)	6174.0(8)
Z	4	8
D_{calcd} [Mg/m^3]	1.868	1.614
cryst dimens [mm^3]	0.26 × 0.20 × 0.12	0.25 × 0.20 × 0.18
θ range for data collecn (deg)	2.10-27.49	2.18-27.51
wavelengths (Å)	0.710 73	0.710 73
reflns collectd	11 100	9574
unique reflns	4046	2872
large diff between peak and hole [e $Å^{-3}$]	+1.409, −0.888	+0.472, −0.332
final R indices [$I > 2\sigma(I)$]		
R1	0.0273	0.0460
wR2	0.0430	0.1138

Experimental Section

A JASCO V-570 spectrometer was used to record electronic spectra. The IR spectra were obtained with a Perkin- Elmer 783 spectrophotometer. ^1H NMR spectra were recorded on a Brucker Avance DPX 300. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N).

Solvents and chemicals used for synthesis were of analytical grade. The ligand HL is prepared following the procedure reported before[4] for similar ligands using 2-aminopyridine as the reagent.

Synthesis of Compounds. (a) [$InCl_3(HL)$]. The ligand HL (100 mg, 0.363 mmol) was dissolved in 25 mL of acetonitrile. To this was added an aqueous solution of $InCl_3{\cdot}4H_2O$ (106 mg (0.363 mmol) in 1 mL of water), and the mixture was stirred for 30 min at room temperature. The color of the solution instantaneously changed from orange to ink blue. The resulting solution was filtered and left undisturbed for slow evaporation. After 24 h, a dark crystalline product deposited in the reaction vessel. These were collected by filtration, cleaned with diethyl ether, and air-dried in a vaccum desiccator. Yield: 50%. Anal. Calcd for $C_{16}H_{13}N_5Cl_3In$: C, 38.67; H, 2.61; N, 14.09. Found: C, 38.65; H, 2.64; N, 14.21.

(b) [$Zn_2Cl_2L_2$]. The ligand HL (100 mg, 0.363 mmol) was dissolved in 25 mL of methanol. To this solution was added an aqueous solution of $ZnCl_2$ (49 mg (0.363 mmol) in 1 mL of water). The mixture was stirred for 30 min at room temperature. The color of the solution changed from orange to ink blue. The resulting solution was filtered and left undisturbed for slow evaporation. A dark crystalline product was deposited in the reaction vessel in about 24 h. This were collected by filtration, cleaned with diethyl ether, and dried. Yield: 55%. Anal. Calcd for $C_{32}H_{24}N_{10}Cl_2Zn_2$: C, 51.18; H, 3.19; N, 18.66. Found: C, 51.27; H, 3.26; N, 18.57.

X-ray Structure Determination. The crystal data of [$InCl_3(HL)$] and [$ZnCl_2L_2$] are collected in Table 3.

(a) [$InCl_3(HL)$]. X-ray quality crystals of [$InCl_3(HL)$] were obtained directly from the reaction mixture. The data were collected on a Bruker SMART diffractometer equipped with Mo Kα radiation (λ = 0.710 73 Å) and were corrected for Lorentz−polarization effects. A total of 11 100 reflections were collected out of which 4046 were unique (R_{int} = 0.0330), satisfying the $I > 2\sigma(I)$ criterion,

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and were used in subsequent analysis. The structure was solved by employing the SHELXS 97 program package[15] and refined by full-matrix least squares based on F^2 (SHELXS 97).[16]

(b) [$Zn_2Cl_2L_2$]. X-ray quality crystals of [$Zn_2Cl_2L_2$] were also obtained from the reaction mixture. The data were collected as noted above. A total of 9574 reflections were collected out of which 2872 were unique ($R_{int} = 0.0467$), satisfying the $I > 2\sigma(I)$ criterion, and were used in subsequent analysis. The structure was solved by employing the SHELXS 97 program package[15] and refined by full-matrix least squares based on F^2 (SHELXS 97).[16]

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Supporting Information Available: X-ray crystallographic details of the two compounds in CIF format, molecular orbital diagrams of [$InCl_3(HL)$]: (a) LUMO; (b) HOMO; (c) HOMO-1. These materials are available free of charge via the Internet at http://pubs.acs.org.

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