Recognition of 1,2-diazines by a bidentate Lewis acid

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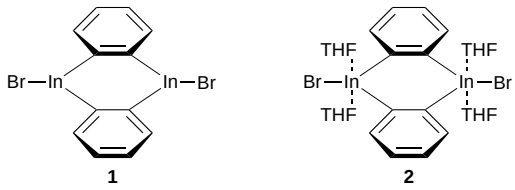
Dimeric *ortho*-phenyleneindium bromide 1 shows a higher affinity for 1,2-diazines than for 1,3- and 1,4-diazines; as shown by the X-ray crystal structure analysis of the host–guest complex 3 the observed selectivity results from subtle structural variation which can bring the indium p orbitals to converge.

The chemistry of group 13-based bidentate Lewis acids, while still in its infancy, appears to have a promising future. Research activity in this area has mainly focussed on the use of these compounds as anion receptors.[1,2] More scarcely, those compounds have been used as catalysts[3,4] or as selective receptors for neutral nucleophiles.[5,6] We have recently reported the synthesis of dimeric *ortho*-phenyleneindium bromide **1**.[7] The specific arrangement of the two indium centers of this derivative indicates that selectivity in the binding of bifunctional bases might be attainable. In order to verify this assumption, we have investigated the ligative behavior of **1** toward the different diazine structural isomers and report that **1** is a selective 1,2-diazine receptor.



1 **2**

Compound **1** was isolated as a tetrakis(tetrahydrofuran) adduct **2**, which dissolves only in polar solvents. Addition of 1 or 2 equiv. of pyrazine (1,4-diazine) or pyrimidine (1,3-diazine) to a [$^2H_8$]THF solution of **2** at 25 °C did not result in any detectable changes of the ^{1}H NMR features of **2** thus indicating weak association between **1** and pyrazine or pyrimidine under those conditions.‡ In contrast, incremental addition of pyridazine (1,2-diazine) or phthalazine (2,3-benzodiazine) to a [$^2H_8$]THF solution of **2** at 25 °C resulted in an up-field shift of the H^{2,3,6,7} NMR resonances of the diindacycle **1** (Fig. 1).‡

These observations reflect the formation of complexes between **1** and the 1,2-diazines (pyridazine or phthalazine). Moreover, the inflection observed in the titration curve of **1** by phthalazine occurs at an added amount of base of one equivalent, thus suggesting the formation of a 1 : 1 host–guest complex, possibly **1**·phthalazine·2THF. Based on this hypothesis, the stability constants of the 1 : 1 complexes **1**·pyridazine·2THF and **1**·phthalazine·2THF can be derived and are respectively equal to 80 ± 10 and 1000 ± 150 M^{-1} (Scheme 1).[8] These data as a whole indicate that **1** is a selective receptor for 1,2-diazines.[9,10]

While the 1 : 1 complex **1**·phthalazine·2THF seems to be the preferred species in solution, colorless pale yellow crystals of the less soluble 1 : 2 complex **1**·2(phthalazine)·THF **3** spontaneously formed in a saturated THF solution containing equimolar amounts of **2** and phthalazine.‡§ Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one solvate THF.¶ As shown in Fig. 2, the diindacycle acts as a ditopic receptor for one phthalazine molecule. Each indium atom adopts a trigonal bipyramidal coordination geometry. As in the parent compound,[7] the equatorial sites are occupied by the two phenylene rings and the bromine atoms. The two nitrogen atoms of the chelated phthalazine molecule [N(21) and N(22)] occupy one of the axial sites of each indium center [In(2) and In(1), respectively]. The coordination sphere of each indium atom is completed by axial ligation of one THF molecule [In(2)] and one phthalazine [In(1)]. The chelation of one phthalazine molecule by the diindacycle has some noteworthy structural consequences. The two indium atoms are displaced towards their respective coordinated nitrogen atoms N(21) and N(22), respectively. As a result, the six-membered ring containing the two indium atoms has a boat-like conformation rather than being planar as in **2**.[7] The two phenylene rings of **3** are not coplanar (dihedral angle of 16.5°) and the dimeric *ortho*-phenylene indium moiety adopts a saddle shape. There is one metrical parameter, which merits comment. The N(22)–In(1) distance [2.824(5) Å] is significantly longer than the other In–N bond lengths observed in **3** [2.398(5) and 2.446(5) Å]. While one could question the existence of a N(22)–In(1) interaction, examination of the bond angles at In(1) and N(22) indicates

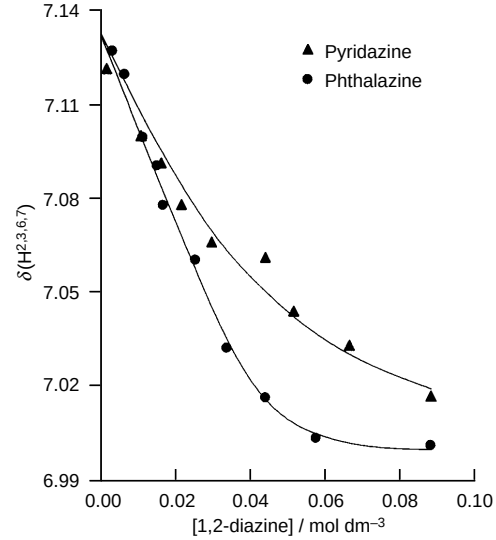
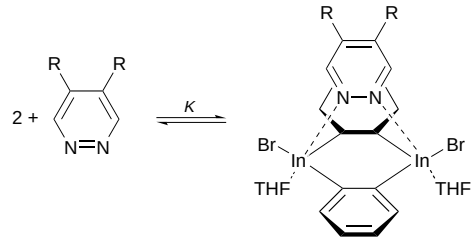


Fig. 1 ^{1}H chemical shift of H^{2,3,6,7} of **1** *vs*. the concentration of 1,2-diazines; [**1**] = 0.044 mol dm^{-3}



R = H, K = 80 M^{-1}
RR = *o*-C_6H_4, K = 1000 M^{-1}

Scheme 1

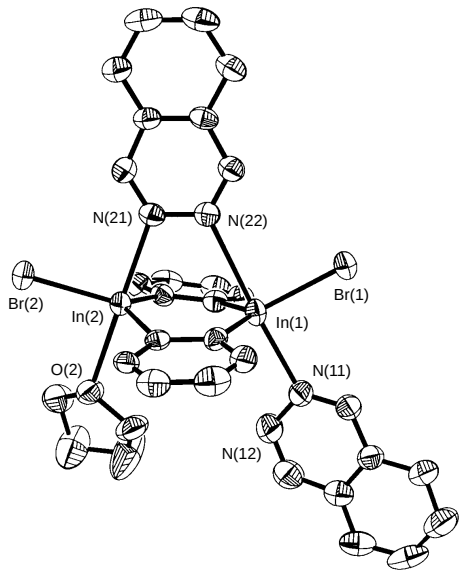


Fig. 2 Structure of **3**. ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): In(2)–O(2) 2.480(4), In(2)–N(21) 2.446(5), In(1)–N(11) 2.398(5), In(1)–N(22) 2.824(5); N(21)–In(2)–O(2) 179.5(2), N(11)–In(1)–N(22) 173.3(2).

clearly that N(22) is positioned at an axial site of the indium coordination sphere. Moreover, the N(22)–In(1) distance is much shorter than the sum of the van der Waals radii [r_{vdw}(N) = 1.5 Å,[11] r_{vdw}(In) = 1.9 Å][12] and just slightly longer than the previously reported longest In–N bond of 2.776 Å.[13] Altogether, these observations suggest the presence of a weak N(22)–In(1) dative bond.

In conclusion, as a result of subtle structural variations, the indium p orbitals of **1** can be brought to converge thus allowing chelation of bifunctional bases with adjacent electrophilic centers. The observed selectivity (phthalazine > pyridazine > pyrimidine ≅ pyrazine) follows the basicity order phthalazine (pK_a 3.5) > pyridazine (pK_a 2.3) > pyrimidine (pK_a 1.23) > pyrazine (pK_a 0.6).[14] It has however been noted previously that pK_a values are poor indicator of the donor ability of nitrogen ligands.[15] Hence, the ability of **1** to chelate 1,2-diazines can be taken as an alternative explanation for the observed selectivity.

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Notes and References

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‡ *^{1}H NMR titration experiment*: incremental addition of pyrazine or pyrimidine (2 × 4 mg, 2 × 50 μmol) to a [$^2H_8$]THF solution (0.5 ml) of **1** (34 mg of **1**·2THF,[7] 50 μmol) did not result in any change of the chemical shift of the aromatic proton signals of either **2** and pyrazine or pyrimidine. The titration curves of **1** by pyridazine and phthalazine were obtained by adding incremental amounts of the 1,2-diazines to a [$^2H_8$]THF (0.45 ml) solution of **1** (14 mg, 20 μmol). After each addition, all solids were brought into solution by gentle heating. Following cooling and before formation of any precipitate, the ^{1}H NMR spectrum of the resulting solution was measured. The stability constant K is defined by K = [Host–Guest]/{[**2**][1,2-diazine]}. The THF concentration is considered as constant and it is therefore not taken into account in the expression of K. *^{1}H NMR data* for **3**: ^{1}H NMR (400 MHz, [$^2H_8$]THF): δ 1.77 (br, 8 H, OCH_2CH_2), 3.61 (br, 8 H, OCH_2), 7.00 (m, 4 H, $H^{2,3,6,7}$), 7.49 (m, 4 H, $H^{1,4,5,8}$), 7.97 (m, 4 H, $H^{5,6}$, phtha), 8.08 (m, 4 H, $H^{8,5}$, phtha), 9.64 (m, 4 H, $H^{1,4}$, phtha).

§ *Synthesis of* **3**: compound **1**·2THF[7] (34 mg, 50 μmol) was dissolved in THF (1 ml) and added to a THF (0.5 ml) solution of phthalazine (6.5 mg, 50 μmol). Crystals of **3** spontaneously precipitated in a 63% yield (15 mg) based on phthalazine [mp 215–255, (decomp)]. Elemental analysis. Calc. for $C_{36}H_{36}Br_2In_2N_4O_2$: C, 45.66; H, 3.80; N, 5.91. Found: C, 45.71; H, 3.83; N, 6.04%.

¶ *Crystal and structure determination data* for **3**: $C_{36}H_{36}Br_2In_2N_4O_2$, M = 946.15, monoclinic, space group $P2_1/n$, a = 10.252(1), b = 18.535(1), c = 19.140(2) Å, β = 99.76(1)°, U = 3584.4(5) Å^3, Z = 4, D_c = 1.753 g cm^{-3}, F(000) = 1856, Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.710 69 Å), T = 21 °C. Data were corrected for Lorentz, polarization, and absorption effects (ψ-scans, $T_{min/max}$ = 83/99%). The structure was solved by direct methods and refined by full-matrix least squares against F^2 (SHELXTL-PLUS, SHELXL-93). Of 6980 measured reflections [$(\sin\theta/\lambda)_{max}$ = 0.62 Å^{-1}], 6902 were used for refinement. The thermal motion of all non-hydrogen atoms was treated anisotropically. All H atoms were calculated in idealized geometry and allowed to ride on their corresponding C atom with U_{iso} = 1.5U_{eq} of the attached C-atom. The structure converged for 415 refined parameters to R_1 = 0.0498 and wR_2 = 0.0930. Residual electron densities: +1.607 and −0.463 e Å^{-3}. CCDC 182/800.

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