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Thermochemistry of some adducts of Indium(III) chloride with neutral donors

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Abstract The $[InCl_3(L)_n]$ (where L is 2,2′-bipyridine (bipy), 2,2′-bipyridine *N*,*N*′-dioxide (bipyNO), *N*,*N*-dimethylacetamide (dma), urea (u), thiourea (tu) or 1,1,3,3-tetramethylthiourea (tmtu); $n = 1.5$, 3 or 4) were synthesized and characterized by melting points, elemental analysis, thermal analysis and IR spectroscopy. The enthalpies of dissolution of the adducts, Indium(III) chloride and ligands in 1.2 M aqueous HCl were measured and by using thermochemical cycles, the following thermochemical parameters for the adducts have been determined: the standard enthalpies for the Lewis acid/base reactions ($\Delta_r H^0$), the standard enthalpies of formation ($\Delta_f H^0$), the lattice standard enthalpies ($\Delta_M H^0$), and the standard enthalpies of decomposition ($\Delta_D H^0$).

Keywords Indium(III) chloride · Thermochemistry · Enthalpies of solution

Introduction

The Indium(III) halides are known to form addition compounds with a variety of donor molecules [1–27]. Many studies have been made on their synthesis, characterization, spectroscopy studies, crystal structure and NMR spectra. The coordination chemistry of Indium(III) halides is continuing interest due in part to the use of such compounds as intermediates in the preparation of the group 13–group 15 semiconductors (InP, etc.). However there is very little information about the energy of the donor–acceptor interaction that is found in the literature [11, 12, 14, 26]. The main purpose of the present work is to fill this lack of information by the calorimetric determination of the energy involved in the formation of some adducts of Indium(III) chloride and also, the determination of several thermochemical parameters for these adducts. It is interesting to know the thermodynamic properties of these compounds that eventually could be useful in determining their potential application in catalysis in different chemical processes. The energy of the interaction between Indium(III) chloride and the ligand determines the rate and direction of the chemical reaction.

Experimental

The ligands 2,2′-bipyridine (99%) [28], 2,2′-bipyridine *N*,*N*′-dioxide (99% +) [29], urea (99%), thiourea (PA) [30], (all from Aldrich Chemical Company), tetramethylthiourea (RP, Fluka) [31], and *N*,*N*-dimethylacetamide (99%, Merck) [27] were purified by methods outlined in the literature. Indium(III) chloride (99% +, Merck) was used as obtained without further purification.

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. The Indium content was determined by complexometric titration with 0.005 M EDTA, using pyridine-2-azo-4-resorcinol as an indicator [8]. Chlorine analysis was obtained by a gravimetric method using standard 0.1 M $AgNO_3$ aqueous solution, after dissolution of the compounds in water [32]. The capillary melting points of the adducts were determined by using a UNIMELT equipment from Thomas Hover.

IR Spectra of adducts and ligands in the solid state were obtained with samples in KBr matrix. For dma, a film of the ligand sandwiched between KBr plates was used. A

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Perkin-Elmer 1600 series FT-IR spectrophotometer in the 4000–400 cm^{-1} region was used. Spectra in the 400–100 cm^{-1} region was obtained with a Bomem FT DA8 spectrophotometer with sample nulls of the adducts in nujol sandwiched between polyethylene plates.

The TG/DTG and DSC measurements were obtained in argon atmosphere in a Du Pont 951 TG analyzer with the samples varying in mass from 3.25 to 14.49 mg (TG/DTG) and from 1.17 to 7.92 mg (DSC) and a heating rate of 10 K min^{-1} in the 298–678 K (DSC) and 298–1248 K (TG/DTG) temperature ranges. Metallic aluminum was used as a standard for the TG calibration for temperatures (mp = 660.37 °C) and the equipment carried out the calibration for mass automatically. Metallic Indium was used as a standard for the DSC calibration (mp = 165.73 ± 1.36 °C, $\Delta_s^l H^\theta = 28.4 \pm 0.21$ J g^{-1}).

All the solution calorimetric measurements were carried out in an LKB 8700-1 calorimeter as described before [29]. The solution calorimetric measurements were performed by dissolving samples of 4.0–46.3 mg of the adducts or Indium(III) chloride in 100 mL of 1.2 M aqueous HCl and the ligands in this last solution maintaining a molar relation salt/ligand equal to the stoichiometry of the adduct.

Results and discussion

All the adducts were obtained in the solid state. The yields range from 39 to 77%. The yields, melting points, colors, appearance and analytical data are summarized in the Table 1. The analytical data suits well with the calculated values for the considered stoichiometry for the compounds. These values were obtained from the atomic and molar mass and the considered general formula.

The more important IR bands of the compounds are reported in the Table 2. The infrared spectra of the bipy adduct shows the appearance of new bands after coordination with relation to the free ligand. Two new bands appear at 1,315 and 732 cm^{-1} due to the adduct formation. This is indication of the coordination of the nitrogen atoms to the Indium atom [33]. The infrared spectra of bipyNO adduct show shifts in frequencies related to the free ligand, of characteristic bands due to the stretching and bending vibrations of the N–O bond (1,300–1,200 and 880–830 cm^{-1} regions). The observed overage shift of the middle point of the first vibration to lower frequencies after coordination is about 48 cm^{-1}. The second vibration is slightly dislocated to lower frequencies. These facts indicate the decrease of the N–O bond order in bipyNO after coordination and are indicative of the coordination of the oxygen atoms of the ligand to the Indium atom [34]. The infrared spectra of the dma adduct show the shifting by 43 cm^{-1} towards higher frequencies of the CO stretching frequency following coordination. The CN stretching frequency also suffered a 12 cm^{-1} shift towards higher frequencies upon coordination [30, 35]. This confirmed the coordination of the ligand to the Indium atom through the oxygen atom. The infrared spectra of the u adduct show a strong band at 1,637 cm^{-1} that is assigned to the C=O stretching vibration. It is observed a shift to lower frequencies with respect to the free ligand. This indicates the coordination of the oxygen atom of the ligand to the Indium atom [36, 37]. For the thio-amide adducts, a strong band is observed in the 1,109–1,086 cm^{-1} region. This is attributed to the C=S stretching frequency [38]. It is observed negative shifts of this frequency in the IR of the adducts with respect to the free ligands, indicating coordination of the ligands through the sulphur atom to the Indium atom [38]. The stretching modes In-Cl and In-L were assigned in the low frequency IR region for all the adducts [2, 6, 10].

The thermogravimetry and derivative thermogravimetry of the bipy adduct shows the loss of part of the ligand in the first step of mass loss following by the decomposition of the intermediate compound in a second step of mass loss, leaving to a residue that is part of the Indium content. The DSC curve is consistent with the TG data and presents an endothermic peak due to the elimination of ligand and a strongly exothermic peak due to the decomposition of the intermediate compound. The TG curve of the bipyNO adduct show the loss of part of the ligand in two steps of mass loss following by the decomposition of the intermediate product in a third step of mass loss leaving to non residue. The DSC curve is consistent with the TG data showing endothermic peaks due to the elimination of

Table 1 Analytical data (in mass %) for the compounds (observed (calculated))

Compound	C	H	N	In	Cl
$[InCl_3(bipy)_{1.5}]$	39.56 (39.11)	2.66 (2.62)	9.23 (9.05)	25.21 (25.31)	23.35 (23.25)
$[InCl_3(bipyNO)_{1.5}]$	35.79 (35.75)	2.40 (2.52)	8.35 (8.50)	22.81 (22.70)	21.13 (21.03)
$[InCl_3(dma)_{1.5}]$	20.48 (20.35)	3.87 (3.95)	5.97 (5.85)	32.63 (32.75)	30.23 (30.30)
$[InCl_3(u)_4]$	10.41 (10.34)	3.50 (3.39)	24.29 (24.17)	24.89 (24.98)	23.05 (23.12)
$[InCl_3(tu)_4]$	9.14 (9.21)	3.07 (2.99)	21.32 (21.52)	21.84 (21.77)	20.23 (20.15)
$[InCl_3(tmtu)_3]$	29.16 (29.00)	5.87 (5.79)	13.60 (13.49)	18.58 (18.61)	17.21 (17.25)

Table 2 Main infrared spectral data (cm^{-1}) for ligands and their adducts

Compound	ν_{NH}	ν_{CO}/ν_{CS}	δ_{NH}	ν_{CC}	ν_{NO}	ν_{CN}	δ_{NO}	ϕ_{CC}	New bands
$[InCl_3(bipy)_{1.5}]$				1596s				772vs	1315m, 732m
$[InCl_3(bipyNO)_{1.5}]$					1217vs, 1204s		846vs, 833vs		
$[InCl_3(dma)_{1.5}]$		1602s				1025m			
$[InCl_3(u)_4]$	3464s, 3357s	1637vs							
$[InCl_3(tu)_4]$	3384s	1086s	1625vs, 1610vs			1497m			
$[InCl_3(tmtu)_3]$		1109s				1382vs			

ligand and an exothermic peak due to the decomposition of the intermediate product. The thermogravimetry of the dma adduct shows the loss of part of the ligand in a first step of mass loss following by the decomposition of the intermediate compound in a second step of mass loss leaving to a residue that is part of the Indium content. The DSC curve is consistent with the TG data and presents a strongly exothermic peak due to the decomposition of the intermediate compound. The TG curve of the u adduct shows the loss of all the ligand in the first step of mass loss following by the decomposition of Indium(III) chloride in more two steps of mass loss leaving to a residue that is part of the Indium content. The DSC curve is consistent with the TG data and presents a strongly exothermic peak due to the decomposition of Indium trichloride. The thermogravimery of the tu adduct shows the loss of the ligand in two steps of mass loss following by the decomposition of Indium(III) chloride in a third step of mass loss leaving to a residue that is part of the Indium content. The DSC curve is consistent with the TG data and presents endothermic peaks due to the elimination of ligand and a strongly exothermic peak due to the decomposition of Indium trichloride. The TG curve of the tmtu adduct shows the loss of part of the ligand in a first step of mass loss following by the decomposition of the intermediate compound in a second step of mass loss leaving to a residue that is part of the Indium content. The DSC curve is consistent with the TG data and presents endothermic peaks due to the elimination of ligand and a strongly exothermic peak due to the decomposition of the intermediate compound leaving to a residue that is part of the Indium content. Brown et al. [9] observed similar behavior for some adducts of Indium(III) halide as was observed here. Figure 1 shows the TG curve of the adduct of tmtu. Figure 2 presents the respective DSC curve.

The standard enthalpies of dissolution of Indium(III) chloride, ligands and adducts were obtained as previously reported [29]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

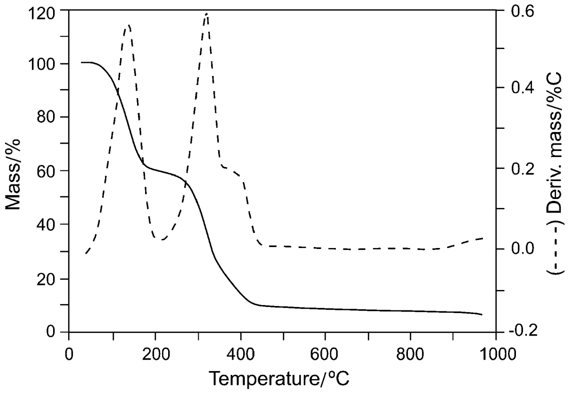

Fig. 1 TG/DTG curve of the adduct $[InCl_3(tmtu)_3]$

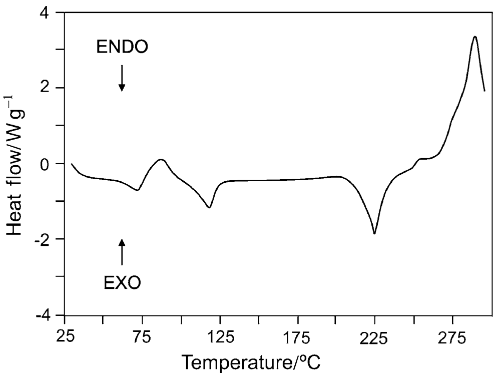

Fig. 2 DSC curve of the adduct $[InCl_3(tmtu)_3]$

$$InCl_{3(s)} + \text{calorimetric solvent} \rightarrow \text{solution A}; \quad \Delta_1 H^\theta \tag{1}$$

$$n\mathrm{L}_{(s,l)} + \text{solution A} \rightarrow \text{solution B}; \quad \Delta_2 H^\theta \tag{2}$$

$$[InCl_3(L)_n]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C}; \quad \Delta_3 H^\theta \tag{3}$$

$$\text{Solution B} \rightarrow \text{solution C}; \quad \Delta_4 H^\theta \tag{4}$$

The application of Hess' law to the series of reactions (1)–(4) gives the standard enthalpies of the acid/base reaction ($\Delta_r H^\theta$) according to the reaction:

Table 3 Standard molar enthalpies (kJ mol^{-1}) of dissolution at 298.15 K

Compound	Calorimetric solvent[a]	Number of experiments	$\Delta_{\mathrm{i}}H_{\mathrm{m}}^{\theta}$
$\mathrm{InCl}_{3(s)}$	HCl in methanol	16	−64.0 ± 0.9
$\mathrm{Bipy}_{(s)}$	1.5:1 InCl_3-HCl in methanol	5	1.0 ± 1.2
$[\mathrm{InCl}_3(\mathrm{bipy})_{1.5}]_{(s)}$	HCl in methanol	4	53.0 ± 1.4
$\mathrm{BipyNO}_{(s)}$	1.5:1 InCl_3-HCl in methanol	5	38.4 ± 0.7
$[\mathrm{InCl}_3(\mathrm{bipyNO})_{1.5}]_{(s)}$	HCl in methanol	4	50.6 ± 1.6
$\mathrm{dma}_{(l)}$	1.5:1 InCl_3-HCl in methanol	4	−8.0 ± 0.9
$[\mathrm{InCl}_3(\mathrm{dma})_{1.5}]_{(s)}$	HCl in methanol	5	12.1 ± 0.5
$\mathrm{tu}_{(s)}$	4:1 InCl_3-HCl in methanol	5	69.0 ± 1.4
$[\mathrm{InCl}_3(\mathrm{tu})_4]_{(s)}$	HCl in methanol	5	57.7 ± 0.7
$\mathrm{u}_{(s)}$	4:1 InCl_3-HCl in methanol	5	41.1 ± 0.7
$[\mathrm{InCl}_3(\mathrm{u})_4]_{(s)}$	HCl in methanol	5	94.1 ± 0.6
$\mathrm{tmtu}_{(s)}$	3:1 InCl_3-HCl in methanol	5	63.1 ± 2.3
$[\mathrm{InCl}_3(\mathrm{tmtu})_3]_{(s)}$	HCl in methanol	5	45.0 ± 1.0

[a] 25% (v/v) 1.2 M aqueous HCl in methanol

Table 4 Summary of the thermochemical results (kJ mol^{-1}) for Indium(III) chloride adducts

Compound	$\Delta_{\mathrm{r}}H^{\theta}$	$\Delta_{\mathrm{f}}H^{\theta}$	$\Delta_{\mathrm{s,l}}^{\mathrm{g}}H^{\theta}$	$\Delta_{\mathrm{M}}H^{\theta}$	$\Delta_{\mathrm{D}}H^{\theta}$
$\mathrm{InCl}_{3(s)}$		−537.2[a]	163.2[a]		
$\mathrm{bipy}_{(s)}$		216.4 ± 7.4[b]	81.93 ± 0.33[b]		
$\mathrm{bipyNO}_{(s)}$		16.6 ± 5.2[c]	180 ± 10[c]		
$\mathrm{dma}_{(l)}$		−278.32 ± 1.50[d]	50.0 ± 0.2[e]		
$\mathrm{u}_{(s)}$		−333.7 ± 0.1[f]	87.2 ± 2.1[f]		
$\mathrm{tu}_{(s)}$		−89.12 ± 0.12[g]	93.7 ± 4.7[h]		
$\mathrm{tmtu}_{(s)}$		−38.3 ± 2.3[i]	93.03 ± 0.20[i]		
$[\mathrm{InCl}_3(\mathrm{bipy})_{1.5}]_{(s)}$	−105.96 ± 2.00	−318.6 ± 11.3		−392.1 ± 2.3	228.86 ± 2.03
$[\mathrm{InCl}_3(\mathrm{bipyNO})_{1.5}]_{(s)}$	−76.25 ± 1.99	−588.6 ± 8.1		−509.5 ± 1.5	346 ± 4
$[\mathrm{InCl}_3(\mathrm{dma})_{1.5}]_{(s)}$	−59.88 ± 1.30	−1014.6 ± 2.8		−298.1 ± 1.7	134.9 ± 1.3
$\mathrm{InCl}_3(\mathrm{u})_4]_{(s)}$	−116.93 ± 1.25	−1988.9 ± 1.7		−631.3 ± 8.6	468.5 ± 8.5
$[\mathrm{InCl}_3(\mathrm{tu})_4]_{(s)}$	−52.70 ± 1.82	−946.4 ± 2.7		−590.7 ± 18.9	27.5 ± 18.9
$[\mathrm{InCl}_3(\mathrm{tmtu})_3]_{(s)}$	−45.91 ± 2.63	−698.0 ± 7.5		−458.2 ± 2.9	295.00 ± 2.69

[a] [40], [b] [29], [c] [41], [d] [42], [e] [43], [f] [44], [g] [45], [h] [46], [i] [47]

$$\mathrm{InCl}_{3(s)} + n\mathrm{L}_{(s,l)} \rightarrow \left[\mathrm{InCl}_3(\mathrm{L})_n\right]_{(s)};\quad \Delta_r H^{\theta} \tag{5}$$

where $\Delta_{\mathrm{r}}H^{\theta} = \Delta_1 H^{\theta} + \Delta_2 H^{\theta} - \Delta_3 H^{\theta}$ since the final thermodynamic state of reactions (2) and (3) is the same and $\Delta_4 H^{\theta} = 0$. Table 3 gives the values obtained for the enthalpies of dissolution of InCl_3 ($\Delta_1 H^{\theta}$), L into the solution of InCl_3 ($\Delta_2 H^{\theta}$) and of the adducts ($\Delta_3 H^{\theta}$). Uncertainty intervals given in this table are twice the standard deviation of the means of 4–16 replicate measurements.

From the values obtained for the standard enthalpies of the acid/base reactions ($\Delta_{\mathrm{r}}H^{\theta}$) and by using appropriate thermochemical cycles [30, 39], the following thermochemical parameters for the adducts were determined: the standard enthalpies of formation ($\Delta_{\mathrm{f}}H^{\theta}$), the standard enthalpies of decomposition ($\Delta_{\mathrm{D}}H^{\theta}$) and the standard lattice enthalpies ($\Delta_{\mathrm{M}}H^{\theta}$). Table 4 lists the values obtained for all these thermochemical parameters.

Conclusions

Based on the $\Delta_{\mathrm{r}}H^{\theta}$ values for the adducts of the same stoichiometry, it is obtained the relative basicity of the ligands: u > tu and bipy > bipyNO. This means that the urea is a better base than thiourea and bipy is a better base than bipyNO, as it would be expected on the basis of an inductive effect according with the electronegative value of the donor atom and also according with the hard/soft acid/base theory (HSAB) [48–50].

The heats of formation of Indium trichloride adducts in the condensed phase are greater for bipyNO than for bipy and greater for u than for tu. Assuming that the heats of sublimation are similar in adducts of the same stoichometry, it appears than oxygen is intrinsically a better donor atom towards Indium(III) chloride than is towards nitrogen or sulphur atoms.

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