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# Analytical and Spectroscopic Study of Indium Extraction with 1,10-Bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1,10-decanedione and Its Mixtures with Tri-*n*-octylphosphine Oxide

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**Summary.** Complex organic phases are obtained by extraction of indium from 1 *M* perchlorate media with chloroform solutions of 1,10-bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1,10-decanedione, "H*L*-8-*L*H". PMR and analytical data show that, at low *pH* and for low extractant concentrations, four extracted species are present: In(*L*-8-*L*) (*L*-8-*L*H), $In_2(L\text{-}8\text{-}L)_3$, $In(L\text{-}8\text{-}LH)_3$ and $In_2(L\text{-}8\text{-}L)_2$ $(L\text{-}8\text{-}LH)_2$. The corresponding extraction constants have been estimated, resp. $0.0 < \log K_{12} < 1.0$; $1.2 < \log K_{23} < 2.2$; $1.0 < \log K_{13} < 2.2$ and $0 < \log K_{24} < 3$. At highest *pH*'s, polymeric species are formed.

The extractible complex $In_2(L\text{-}8\text{-}L)_3$ has been synthesized. It contains two "(*L*-8-*L*)In" moieties where $L\text{-}8\text{-}L^{2-}$ acts as a bis-chelatant folded on the indium atom, linked by a $L\text{-}8\text{-}L^{2-}$ bridge. This complex slowly rearranges in chloroform solutions to form polymeric species.

A weak synergy is observed by adding tri-*n*-octylphosphine oxide, "*TOPO*", to the extraction solvent. The organic extraction phase mainly contains $In_2(L\text{-}8\text{-}L)_3$ $(TOPO)_2$. The corresponding extraction constant is $\log K_{232} = 6.6 \pm 0.2$. $^{31}P$-NMR shows that this complex is not formed by *TOPO* addition in the organic phase, contrary to the usual description of the synergistic effect.

**Keywords.** Bis(4-acylpyrazol-5-ol) derivative; Liquid-liquid extraction; Synergy; NMR, Indium complex.

## Analytische und spektroskopische Untersuchung der Extraktion von Indium mittels 1,10-Bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1,10-decandion und dessen Mischungen mit Tri-*n*-octylphosphinoxid

**Zusammenfassung.** Die Extraktion von Indium aus Perchlorat-Lösungen mittels 1,10-Bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1,10-decandion, „H*L*-8-*L*H", in Chloroform führt zu komplexen organischen Phasen. Protonen-Kernresonanz und analytische Daten zeigen, daß bei niedrigem *pH* und schwachen Konzentrationen an Extraktionsmittel vier extrahierte Verbindungen vorhanden sind: In(*L*-8-*L*) (*L*-8-*L*H), $In_2(L\text{-}8\text{-}L)_3$, $In(L\text{-}8\text{-}LH)_3$ und $In_2(L\text{-}8\text{-}L)_2$ $(L\text{-}8\text{-}LH)_2$. Die entsprechenden Extraktionskonstanten wurden auf $0.0 < \log K_{12} < 1.0$; $1.2 < \log K_{23} < 2.2$; $1.0 < \log K_{13} < 2.2$ und $0 < \log K_{24} < 3$ geschätzt. Bei höherem *pH* bilden sich polymere Verbindungen.

Der extrahierbare Komplex $In_2(L\text{-}8\text{-}L)_3$ wurde unabhängig synthetisiert. Er enthält zwei „(*L*-8-*L*)In"-Gruppen, in denen $L\text{-}8\text{-}L^{2-}$ als ein Bis-Chelat-Ligand um das Indium-Atom gefaltet ist, und die durch eine $L\text{-}8\text{-}L^{2-}$-Brücke verbunden sind. Dieser Komplex wandelt sich in Chloroform-Lösungen langsam in polymere Verbindungen um.

Bei Zusatz von Tri-*n*-octylphosphinoxid („*TOPO*“) zum Extraktionsmittel wird ein schwacher Synergismus beobachtet, wobei die organische Phase hauptsächlich $In_2(L\text{-}8\text{-}L)_3\ (TOPO)_2$ enthält. Die entsprechende Extraktionskonstante war $\log K_{232} = 6.6 \pm 0.2$.

Die $^{31}P$-Kernresonanz zeigt, daß dieser Komplex nicht durch *TOPO*-Addition in der organischen Phase gebildet wird, im Gegensatz zu den üblichen Annahmen über Prozesse mit synergistischem Effekt.

## Introduction

From the study of the extracting and complexing properties of bis(4-acyl-5-pyrazolols) derivatives, "H*L*-*n*-*L*H", in which the two chelatant groups are linked by a polymethylene chain (Fig. 1), these species appear to be better extractants than

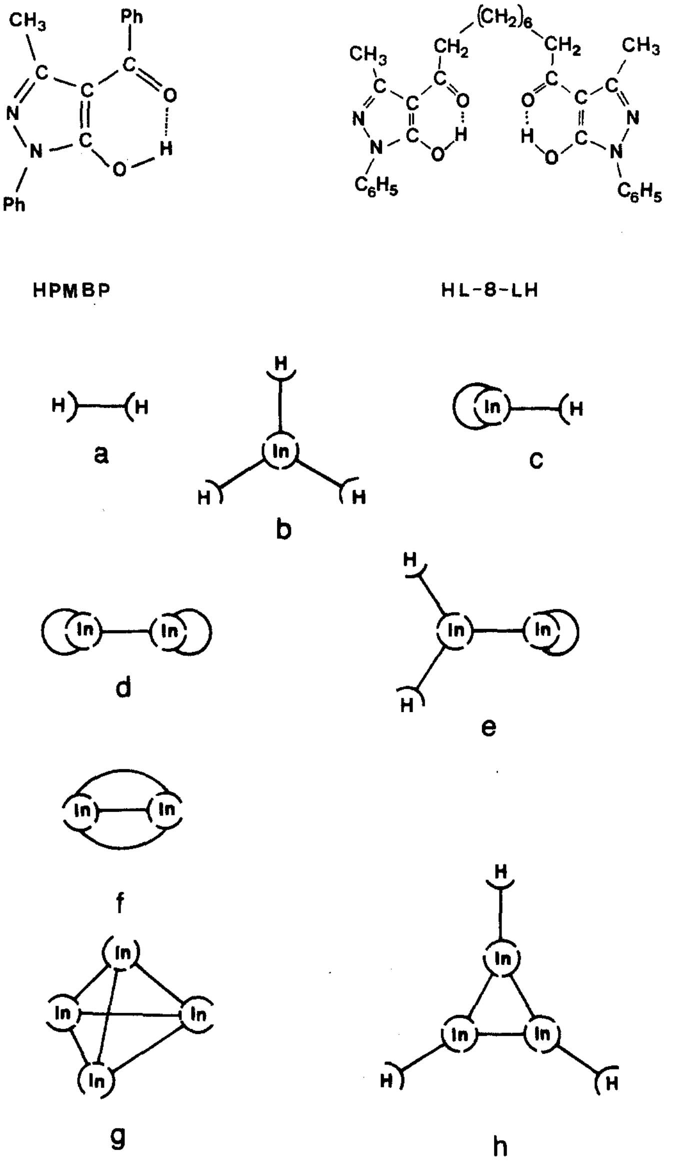

**Fig. 1.** The extractants and some possible extractable complexes

the "parent compounds", 4-acyl-5-pyrazolols (e.g. H*PMBP*, see Fig. 1), owing to the better lipophilicity of the extracted complexes. The polymethylene chain length influences both the overall extraction yield and the nature of the extracted species. Most often, a better extraction is observed with H*L*-8-*L*H [1 – 3]. For a given extractant ($n=8$) the complexes $M(L\text{-}8\text{-}L)$, $M_2(L\text{-}8\text{-}L)_2$ and $M(L\text{-}8\text{-}L\mathrm{H})_2$ are extracted respectively for the divalent ions $\mathrm{Cu}^{2+}$, $\mathrm{Co}^{2+}$ and $\mathrm{Zn}^{2+}$ [4, 5]. For a given ion, $\mathrm{Cu}^{2+}$, $\mathrm{Cu}_2(L\text{-}n\text{-}L)_2$ complexes are extracted for $n=1$ to 7, $\mathrm{Cu}(L\text{-}n\text{-}L)$ for $n \geqslant 8$, and, for $n=2$ or 4, $\mathrm{Cu}(L\text{-}n\text{-}L\mathrm{H})_2$ species are also observed when very diluted solutions of copper are used [2]. This behaviour is obviously due to the ability of $L\text{-}n\text{-}L^{2-}$ to form two chelate rings by folding on the same metallic center, which depends on the chain length and the radius of the coordinated ion.

In this respect, it is worth studying the extraction of a trivalent ion which might form various kind of complexes (see Fig. 1). $\mathrm{In}^{3+}$ was chosen to allow comparison with divalent $\mathrm{Zn}^{2+}$ [5] and $\mathrm{Cd}^{2+}$ (work in progress), since its ionic ratio stands between theirs. Moreover, its extraction by 4-acyl-pyrazol-5-ols was extensively studied in our laboratory [6, 7] and, since it is diamagnetic, NMR data which would give a better comprehension of the systems can be easily obtained.

## Experimental Part

Inorganics were Prolabo or Merck analytical grade products. Solvents were purchased from Prolabo ("Rectapur" quality) or Fluka ("für die Spektroskopie"). Tri-*n*-octylphosphine oxide ("*TOPO*") was a Merck (purum) product purified by washing of its chloroform solution with aqueous alkali carbonate and recrystallization. The deuterated solvents were obtained from the French CEA (Atomic Energy Agency, Saclay). These were used without further purification. 1,10-Bis[1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl]-1,10-decanedione ("H*L*-8-*L*H") was prepared by Jensen's method [8] and recrystallized three times in a chloroform-ethanol mixture.

### *Extraction and Analytical Procedures*

(Overlined symbols refer to the organic phase, the index "*i*" denotes initial concentration before contacting the phases).

Unless otherwise noted, the initial composition of the phases were as follows. Aqueous phase: $[\mathrm{In}]_i=4.35\cdot10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[(\mathrm{Na,H})^+\mathrm{ClO_4}^-]=1\,\mathrm{mol\,dm^{-3}}$, $pH=0.6$ to 2. Organic phase: $\mathrm{CHCl_3}$ saturated with the blank (i.e. without $\mathrm{In}^{3+}$) aqueous phase, $\overline{[\mathrm{chelatant}]}_i=10^{-2}\,\mathrm{mol\,dm^{-3}}$, $\overline{[\mathrm{solvant}]}_i=10^{-2}\,\mathrm{mol\,dm^{-3}}$, if any. The distribution measurements were performed using a batch technique in thermostated vessels, at 25 ± 0.2°C. Equal volumes of the two phases were contacted under magnetic stirring and then separated by gravity. For each experimental point, aliquots of the two phases were drawn and the metal was stripped from the organic aliquot with 1 *M* aqueous HCl. Indium concentrations were determined by flame atomic absorption, using a Perkin-Elmer 2380 AA spectrophotometer.

Kinetic tests were performed for extreme *pH*'s and concentrations of the extractants, and for "typical" extraction systems: $pH\,1$, $\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}_i$ $10^{-2}M$; $pH\,1$, $\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}_i$ $10^{-2}M$, $\overline{TOPO}_i$ $10^{-2}M$. Aliquots of the solutions were drawn every 5 min during 120 min. It was shown that the organic and aqueous concentrations of indium remain constant (within the experimental error) after 20 – 35 min. Thus the contacting time of the phase was set at 40 min.

### *Synthesis of* $\mathrm{In}_2(L\text{-}8\text{-}L)_3$

H*L*-8-*L*H in ethanol (0.01 *M*) and aqueous $\mathrm{InClO_4}$ (0.05 *M*) were mixed in stoichiometric proportions and the resulting solution reduced to 1/5 th by vacuum evaporation (≈ 0.2 mm Hg, 50°C). The resulting solid was filtered, washed several times with warm ethanol and then with water, dried (≈ 0.2 mm Hg, 50°C) and kept in a desiccator.

N, C and H analyses were performed by the French CNRS Analysis Service (Solaize). For indium determination, the complex was mineralized with concentrated $HNO_3$ before dilution and atomic absorption determination. Calc. for $In_2(L\text{-}8\text{-}L)_3$: C 61.16, H 5.47, N 9.51, In 12.99. Exp.: C 61.21, H 5.43, N 9.52, In 12.9%.

The mass spectrum agrees with a dimeric structure.

### *Spectroscopic Measurements*

IR spectra were recorded on a Perkin-Elmer 457 spectrometer. The samples were pelletized in KBr or pressed between KBr plates as hexachlorobutadiene mulls.

NMR spectra were recorded on a Bruker WP-200 FT-spectrometer (4.7 T field). Standard conditions were used for PMR. Pulse and acquisition parameters for $^{31}$P-NMR were: pulse width 4.0 μs, acquisition time: 2.28 s, relaxation delay: 0.0 s, broad band $^1$H decoupling. Some PMR spectra were recorded on a Bruker AM 400 FT-spectrometer (9.4 T field), to allow a better resolution.

## Results and Discussion

### *The Indium(III) / HL-8-LH System*

### Slope Analysis of the Extraction Curves

The main extraction results (Fig. 2) show a log $D$ vs. $pH$ dependence approximately linear, with slopes $\approx 2.5$ for curve 2A to $\approx 3.7$ for curve 2C, i.e. the mean slope increases with the extractant initial concentration. This gives evidence of the occurrence of more than one extraction equilibrium. The high slope of curve 2C shows that di- or polynuclear metallic species are probably involved in the process. This is confirmed by the observed dependence of the distribution coefficient on the initial concentration of indium, as shown by some tests. The unexpected curvature and mean slope of curve 2A (2.5, i. e. less than the valency of the extracted metal)

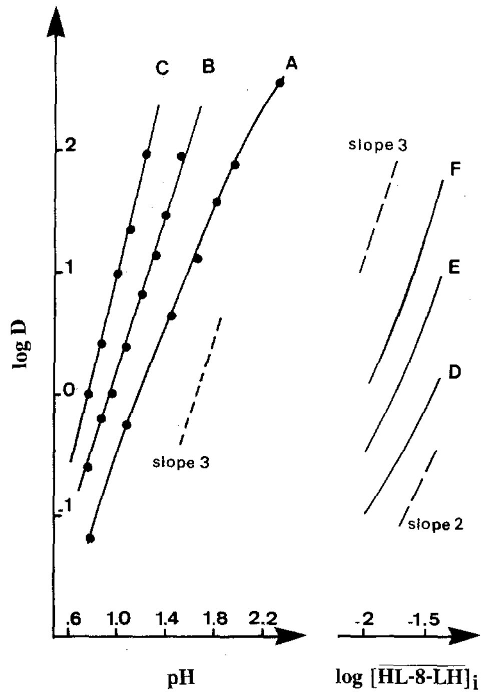

**Fig. 2.** Extraction of indium from 1 $M$ perchlorate media with HL-8-LH in chloroform. $[HL\text{-}8\text{-}LH]_i$: $10^{-2} M$ ($A$); $2 \cdot 10^{-2} M$ ($B$); $4 \cdot 10^{-2} M$ ($C$). $pH = 0.8$ ($D$); 1.0 ($E$); 1.2 ($F$)

are due to the decrease of the free extractant concentration $[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]$ with respect to its initial value $[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i$ by complexation upon indium: since $[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i$ is only 2.3 times higher than $[\mathrm{In}]_i$, this decrease is not at all negligible for medium or high distribution coefficients.

Studies about zinc extraction and coordination by H*L*-8-*L*H [5] showed that this ligand can act as a mono-chelatant (bidentate) or as a bis-chelatant (tetradentate) upon zinc. Thus, one cannot "a priori" exclude any of the structures in Fig. 1. They correspond to the following extraction equilibria:

$$\mathrm{In}^{3+} + 3\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}(L\text{-}8\text{-}L\mathrm{H})_3} + 3\mathrm{H}^+, \quad \text{cnt}{:}\,K_{13}, \tag{1}$$

$$\mathrm{In}^{3+} + 2\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})} + 3\mathrm{H}^+, \quad \text{cnt}{:}\,K_{12}, \tag{2}$$

$$2\,\mathrm{In}^{3+} + 3\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}_2(L\text{-}8\text{-}L)_3} + 6\mathrm{H}^+, \quad \text{cnt}{:}\,K_{23}, \tag{3}$$

$$2\,\mathrm{In}^{3+} + 4\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}_2(L\text{-}8\text{-}L)_2(L\text{-}8\text{-}L\mathrm{H})_2} + 6\mathrm{H}^+, \quad \text{cnt}{:}\,K_{24}, \tag{4}$$

$$2\,\mathrm{In}^{3+} + 5\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}_2(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})_4} + 6\mathrm{H}^+, \quad \text{cnt}{:}\,K_{25}, \tag{5}$$

$$u\,\mathrm{In}^{3+} + (v+w)\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} \leftrightarrows \overline{\mathrm{In}_u(L\text{-}8\text{-}L)_v(L\text{-}8\text{-}L\mathrm{H})_w} + 3u\,\mathrm{H}^+, \text{cnt}{:}\,K_{u,\,v+w}, \tag{6}$$

with $v+w > 1.5\,u$. The distribution coefficients are:

$$D_{12} = \overline{[\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})]}\,/\,[\mathrm{In}], \qquad D_{13} = \overline{[\mathrm{In}(L\text{-}8\text{-}L\mathrm{H})_3]}\,/\,[\mathrm{In}],$$

$$D_{23} = 2\,\overline{[\mathrm{In}_2(L\text{-}8\text{-}L)_3]}\,/\,[\mathrm{In}], \qquad D_{24} = 2\,\overline{[\mathrm{In}_2(L\text{-}8\text{-}L)_2(L\text{-}8\text{-}L\mathrm{H})_2]}\,/\,[\mathrm{In}],$$

$$D_{25} = 2\,\overline{[\mathrm{In}_2(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})_4]}\,/\,[\mathrm{In}],$$

$$D_{u,\,v+w} = u\,\overline{[\mathrm{In}_u(L\text{-}8\text{-}L)_v(L\text{-}8\text{-}L\mathrm{H})_w]}\,/\,[\mathrm{In}].$$

From mass-action law, one can write:

$$\log D_{13} = \log K_{13} + 3pH + 3\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}], \tag{7}$$

$$\log D_{12} = \log K_{12} + 3pH + 2\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}], \tag{8}$$

$$\log D_{23} = \log K_{23} + 6pH + 3\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] + \log 2 + \log[\mathrm{In}], \tag{9}$$

$$\log D_{24} = \log K_{24} + 6pH + 4\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] + \log 2 + \log[\mathrm{In}], \tag{10}$$

$$\log D_{25} = \log K_{25} + 6pH + 5\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] + \log 2 + \log[\mathrm{In}], \tag{11}$$

$$\begin{aligned}\log D_{u,\,v+w} = {} & \log K_{u,\,v+w} + 3upH + (v+w)\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] + \log u \\ & + (u-1)\log[\mathrm{In}],\end{aligned} \tag{12}$$

hence

$$\log(D_{23}\,/\,2[\mathrm{In}]) = \log K_{23} + 6pH + 3\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}], \tag{13}$$

$$\log(D_{24}\,/\,2[\mathrm{In}]) = \log K_{24} + 6pH + 4\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}], \tag{14}$$

$$\log(D_{25}\,/\,2[\mathrm{In}]) = \log K_{25} + 6pH + 5\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}], \tag{15}$$

$$\log(D_{u,\,v+w}/u[\mathrm{In}]^{u-1}) = \log K_{u,\,v+w} + (3u)pH + (v+w)\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]. \tag{16}$$

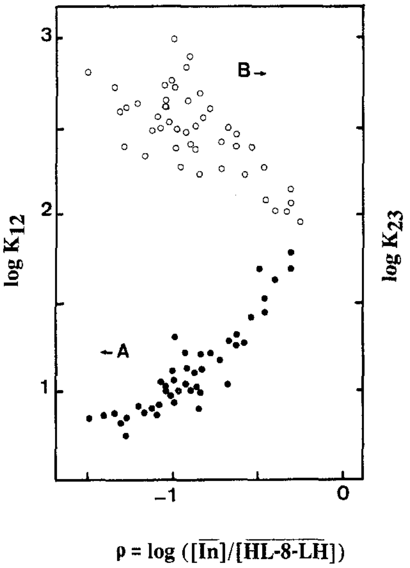

**Fig. 3.** Extraction quotients calculated by using the assumption that only one species is extracted. *A*: In($L$-8-$L$)($L$-8-$L$H); *B*: $\mathrm{In}_2(L\text{-}8\text{-}L)_3$

The curve 2D (Fig. 2) shows that at low *pH* the $\log D$ dependence vs. $\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i$ is near 2, like in Eq. (8). This means that the equilibrium (2) probably occurs. However, since the slopes of 2E and 2F reach and even exceed 3, Eq. (1) is not excluded.

From the preceding experimental data, curves $\log(D/2[\mathrm{In}])$ vs. *pH* and vs. $\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i$ have been drawn to test Eqs. (12) to (15). At low *pH*, the slopes of the curves $\log(D/2[\mathrm{In}])$ vs. $\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i$ are close to 3, which means that, among the dinuclear species, $\mathrm{In}_2(L\text{-}8\text{-}L)_3$ is probably the main extracted species. However, for higher *pH* and/or extractant concentrations, these slopes reach 5.6, which means that equilibria (4) and (5) cannot be excluded and that polynuclear species certainly play a role in the extraction.

As a first approximation, it was assumed that, within particular experimental conditions, the only extracted species is either $\mathrm{In}_2(L\text{-}8\text{-}L)_3$ or $\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})$. Thus, for each experimental point, $\log K_{12}$ and $\log K_{23}$ were calculated from Eqs. (8) and (9). In Fig. 3 those values are reported vs. $\rho = \log([\mathrm{In}]/[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i)$: in the organic phase, $\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})$ would be favoured if H$L$-8-$L$H is in excess with respect to indium (i. e. low values of ρ), and $\mathrm{In}_2(L\text{-}8\text{-}L)_3$ would be favoured in the opposite case. Indeed, $\log K_{12}$ is rather constant (ca. 0.9) for $\rho < -1.1$, while $\log K_{23}$ might tend towards ca. 2.1 for $\rho > -0.2$. However, one cannot obtain a good fit between the calculated and the experimental values when using this model. Hence, the extrapolated values of $\log K_{12}$ (0.9) and $\log K_{23}$ (2.1) must be considered as upper limits and the simultaneous occurrence of other extracted species, in non-negligible amounts, is suggested.

## Preparation and Study of an Extractable Complex

As it was emphasized by some authors [9], the slope analysis method is limited for the interpretation of complex systems. Complementary techniques are required. Therefore, spectroscopic studies were planned. With this aim, attempts were made to prepare solid indium-extractant complexes as references for these studies. As

**Table 1.** $^1$H NMR spectra (in parentheses: coupling constants (Hz), in brackets: relative intensities)

| Samples (in CDCl$_3$) | H$_o$ | H$_m$ | H$_p$ | CH$_3$ | CH$_{2,\alpha}$ | CH$_{2,\beta}$ | CH$_{2,\gamma\delta}$ | Assignments |
|---|---|---|---|---|---|---|---|---|
| H*PMLP* | 7.84 | 7.45 | 7.28 | 2.48 | 2.74 | 1.75 | 1.27 | H*L'* |
| H*L*-8-*L*H | 7.83 | 7.46 | 7.28 | 2.49 | 2.75 (7.4) | 1.76 | 1.40 | H*L*-8-*L*H |
| Zn (*L*-8-*L*) (H$_2$O) | 7.84 | 7.37 | $\simeq$7.17 | 2.47 | 2.74$^a$ | 1.71 | 1.39 | *L*-8-*L* folded around Zn |
| Zn (*L*-8-*L*) (H$_2$O) + 30 *TOPO* | 8.14 | 7.38 | $\simeq$7.15 | 2.44 | 2.75$^a$ | hidden | hidden | Zn (*L*-8-*L*) (*TOPO*); *L*-8-*L* folded, tightly bound |
| | 7.83 | 7.45 | $\simeq$7.28 | 2.48 | 2.75 | hidden | hidden | Zn (*L*-8-*L*) (*TOPO*)$_2$; *L*-8-*L* folded, loosely bound |
| In$_2$ (*L*-8-*L*)$_3$ just dissolved | 7.86 (8.3) | 7.34 (8.2) | 7.18$_6$ (7.4) | 2.38 [1] | 2.68 (7.5) | 1.61 (7.4) | 1.43, 1.21 | *L*-8-*L* bridge |
| | 7.82$_1$ (8.3) | 7.30 (8.2) | 7.14$_5$ (6.8) | 2.42 [2] | 2.80$^a$ | 1.67 | 1.48, 1.28 | *L*-8-*L* folded |
| other signals after 3 days | 7.81$_6$ (7.6) | 7.31 (7.9) | 7.16 (7.4) | 2.43 | 2.77 (6.8) | 1.69 (6.6) | 1.48, 1.37 | supplementary bridges for polymeric species |
| Freshly prepared organic extraction phases (with *TOPO*) | $\simeq$7.82 ($\simeq$8) | 7.30 (8.2) | $\simeq$7.15 ($\simeq$7) | 2.38 [1] | 2.68 (7.5) | hidden by *TOPO* peaks | hidden | In$_2$ (*L*-8-*L*)$_3$ (*TOPO*)$_2$ |
| | | | | 2.42 [2] | 2.78$^a$ | | | |
| | $\simeq$7.81$_5$ ($\simeq$8) | + | + | 2.43 [0.4] | 2.80 (7) | | | |
| | 7.86 ($\simeq$8) | others | others | 2.46 [0.08] | | | | polymeric species |

[a] Special shape (see text)

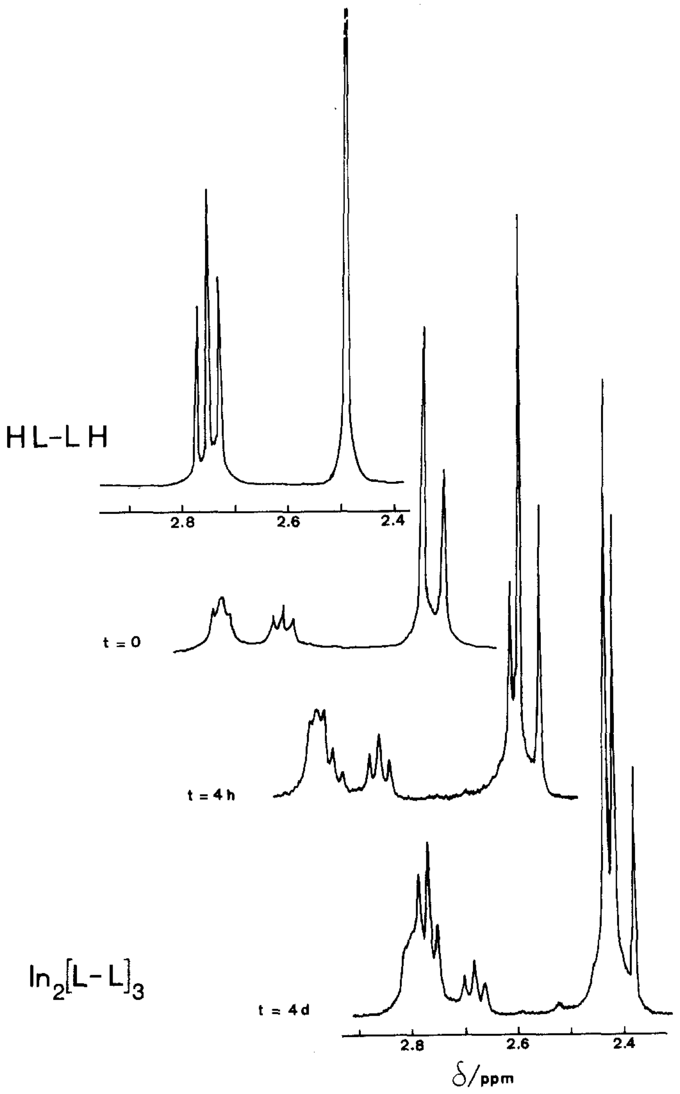

**Fig. 4.** Some reference $^1$H-NMR spectra. $^1$H frequency: 400 MHz; solvent $CDCl_3$

shown in the experimental part, only one complex was obtained, corresponding to the formula $In_2(L\text{-}8\text{-}L)_3$. Its IR spectrum resembles that of $Zn(L\text{-}8\text{-}L)(H_2O)$ [5] and other metallic complexes of H*L*-8-*L*H [3]: it clearly shows that the ligand acts as a chelating agent. Its NMR spectrum in $CDCl_3$ (see Table 1 and Fig. 4) looks like the superimposition of the spectra of two "*L*-8-*L*" moieties in a 2 : 1 ratio. This agrees with a molecular structure where one *L*-8-*L* moiety forms a bridge between the two indium centers, while each of the other ones is tetracoordinated on one indium atom (Fig. 1, d). Indeed, the signal corresponding to the $CH_{2,\ \alpha}$ protons of the major *L*-8-*L* moiety (2.8 ppm, see Fig. 4) does not appear as a 1 : 2 : 1 triplet but in a shape characteristic of restricted rotation. Therefore, like in the complex $Zn(L\text{-}8\text{-}L)(H_2O)$, the $\text{-}(CH_2)_8\text{-}$ chain is long enough to allow the folding of one ligand around the metallic center, with some steric constraint. It is noticeable that in chloroformic solution the complex remains no longer stable: a new set of signals, corresponding to a new "*L*" appears and grows with time, while the 2 : 1

ratio of the above signals is maintained. The shape of the $CH_{2,\alpha}$ protons at 2.77 ppm, a 1 : 2 : 1 triplet, is that of an unstrained chain. Therefore, it may correspond to an "all-bridged" complex of formula $[In_2(L\text{-}8\text{-}L)_3]_n$, for example $In_2(L\text{-}8\text{-}L)_3$ (Fig. 1, f), $In_4(L\text{-}8\text{-}L)_6$ (Fig. 1, g), etc.

## $^1$H-NMR Spectroscopy of Some Extraction Phases

The PMR spectra of three extraction phases were recorded first extemporaneously (Fig. 5) and then after three days. They mainly show the complexity of the extraction phases: note that in Fig. 5 each peak of the "multiplet" between 2.3 and 2.55 ppm ($CH_3$-pyrazole protons) corresponds to one kind of "$L$". An evolution with time is also observed (see below).

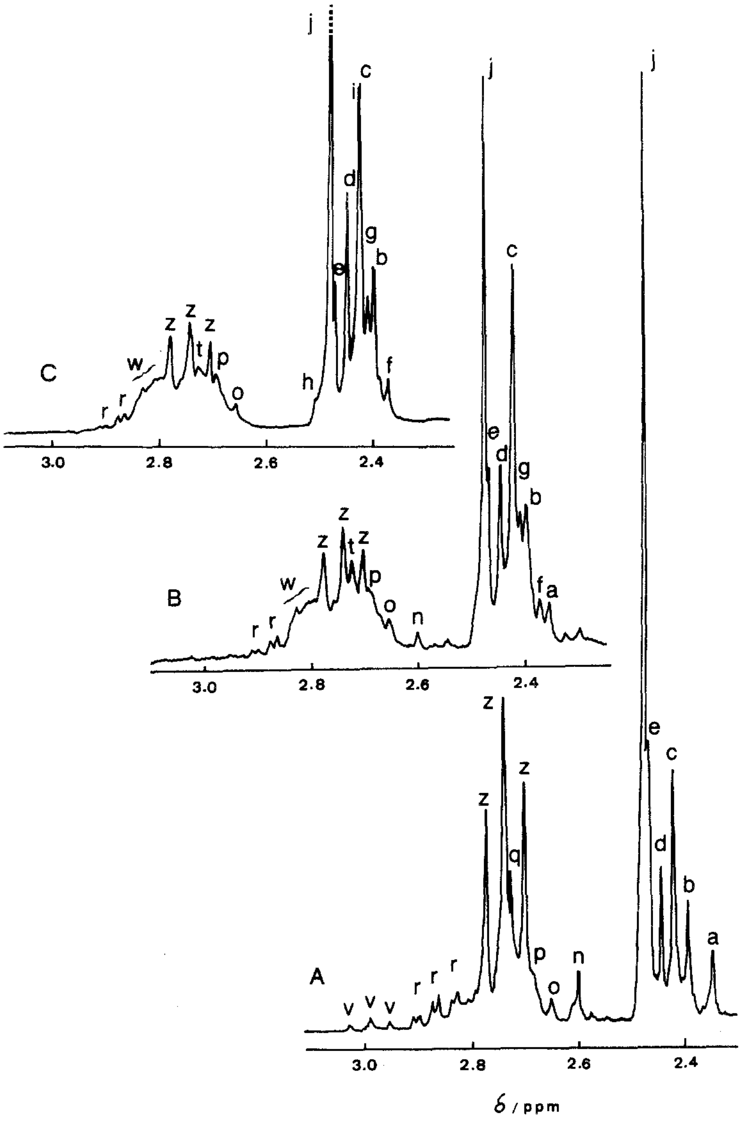

**Fig. 5.** PMR spectra of extraction organic phases. $In^{3+}$, $(Na, H)^+ClO_4^-$ 1 $M$ in $D_2O/HL\text{-}8\text{-}LH$ $10^{-2}$ $M$ in $CDCl_3$. $A$: $pH = 1.0$; $B$: $pH = 1.9$; $C$: $pH = 2.3$. $^1$H frequency 200 MHz

The signals j ($CH_3$, sg) and z ($CH_{2,\alpha}$, tr) are obviously due to the free extractant. The singulet c and two complex $CH_{2,\alpha}$ signals, the first one hidden near 2.72 ppm, the other one near 2.80 ppm (w) likely correspond to ligands tetracoordinated (folded) upon one indium atom. They grow from *pH* 1.06 to *pH* 1.9. w and part of c are attributed to $In_2(L\text{-}8\text{-}L)_3$, the main other species might be $In(L\text{-}8\text{-}L)(L\text{-}8\text{-}LH)$. The percentage of the former species grows with time. The singlet e, which decreases with increasing extraction *pH*, might be attributed to the "-*L*H" terminal moieties. The signals a, b and d might be due to "*L*" moieties coordinated upon one indium atom, in a non-folded ligand: at *pH* 1.06, b corresponds to $In_2(L\text{-}8\text{-}L)_3$, the signal a might be attributed to $In(L\text{-}8\text{-}LH)_3$ since it disappears at high extraction, i. e. when the free ligand/organic indium becomes low, and d might correspond to $In(L\text{-}8\text{-}L)(L\text{-}8\text{-}LH)$. At higher *pH*, the appearance of peaks f, g, h, i likely corresponds to condensed species.

A more precise interpretation would need a great many spectra, with a better resolution, to allow the integration of the signals, to precise the variation of their intensities with *pH*, and thus to unambiguously correlate the position of all the peaks of the individual species. Already at this stage, however, evidence is given of the occurrence of a number of extracted species, among them $In_2(L\text{-}8\text{-}L)_3$, and most probably $In(L\text{-}8\text{-}L)(L\text{-}8\text{-}LH)$ and $In(L\text{-}8\text{-}LH)_3$, in agreement with the preceding analysis of the extraction data.

## Estimation of the Extraction Constants

Given a set of extraction constants and the experimental conditions corresponding to one experimental point ($[\overline{HL\text{-}8\text{-}LH}]_i$, $[In]_i$, *pH*), and assuming that $[\overline{HL\text{-}8\text{-}LH}]_i = [\overline{HL\text{-}8\text{-}LH}]$, one can easily calculate the indium concentration in both phases $[In]_c$ and $[\overline{In}]_c$, and, hence $D_c = [\overline{In}]_c/[In]_c$. It is also possible to take into account the difference between $[\overline{HL\text{-}8\text{-}LH}]$ and $[\overline{HL\text{-}8\text{-}LH}]_i$, which leads to more tedious iterative calculations. If all the extraction constants in the given set are the real ones, $D_c$ must equal $D_{exp}$ and $\Delta D = D_{exp} - D_c$ must be zero. This must also be true for the other experimental points.

Taking into account the experimental points corresponding to the lowest values of *pH* (*pH* < 1.25) and $[\overline{HL\text{-}8\text{-}LH}]_i$, and the most probable extractable species (i. e. corresponding to the equilibria 1 to 5), two series of calculations were carried out:

- calculations with sets of two or three constants among $K_{13}$, $K_{12}$, $K_{23}$;
- calculations with sets of five constants: $K_{13}$, $K_{12}$, $K_{23}$, $K_{25}$, and $K_{24}$.

The results obviously show that the system is undetermined: zero values are obtained for an infinity of sets of constants. However, some conclusions can be drawn:

- the equilibrium corresponding to $K_{25}$, i.e. to the extracted complex $In_2(L\text{-}8\text{-}L)(L\text{-}8\text{-}LH)_4$, is negligible;
- $\log K_{12} < 1.0$; $\log K_{23} < 2.2$; $\log K_{13} < 2.2$; $0.0 < \log K_{24} < 3.0$.

From the NMR data, it is known that at low *pH* at least five different "*L*" moieties exist in the diverse extracted complexes and that the complexes $In(L\text{-}8\text{-}L)_3$, $In(L\text{-}8\text{-}L)(L\text{-}8\text{-}LH)$ and $In_2(L\text{-}8\text{-}L)_3$ occur simultaneously in the extraction.

Therefore, the lower values of constants $K_{12}$, $K_{13}$, and $K_{23}$ that lead to no effect upon the system may be eliminated. Hence, we might propose the following orders of magnitude:

$$1.0 < \log K_{13} < 2.2, \qquad 0.0 < \log K_{12} < 1.0,$$
$$1.2 < \log K_{23} < 2.2, \qquad 0.0 < \log K_{24} < 3.0.$$

Thus, even in the "simpler" low-*pH* case, the system is so complex that the treatment of the analytical data does not lead to an unambiguous solution. This might be due to the insufficient precision of indium determinations. Moreover, erroneous conclusions may be drawn: for example, by testing only a few set of equilibrium constant values, one might find a possible solution, among an infinity, and consider it as the single one. In this respect, a complementary technique may be very useful. The few PMR data obtained show that the extraction phases are complex ones, even at low *pH*, so that too simple interpretations of the analytical data have to be rejected. Moreover, they allow us to propose less unprecise values for the order of magnitude of the extraction constants.

### *The Indium(III)/*H*L*-8-*L*H + TOPO *System*

The extraction curves (Fig. 6 and 7) show a rather weak synergistic effect of *TOPO*, $\Delta \log D$ ca. 0.4 for $10^{-2} M$ *TOPO*, compared with the extraction of zinc with the same extractant ($\Delta \log D$ ca. 2 under comparable conditions) and that of indium with 4-acylpyrazol-5-ols ($\Delta \log D$ ca. 1.2). Very often, these are far from straight lines with integer slopes, showing that the extraction process is a complex one. Some measurements also showed that the extraction depends upon the initial con-

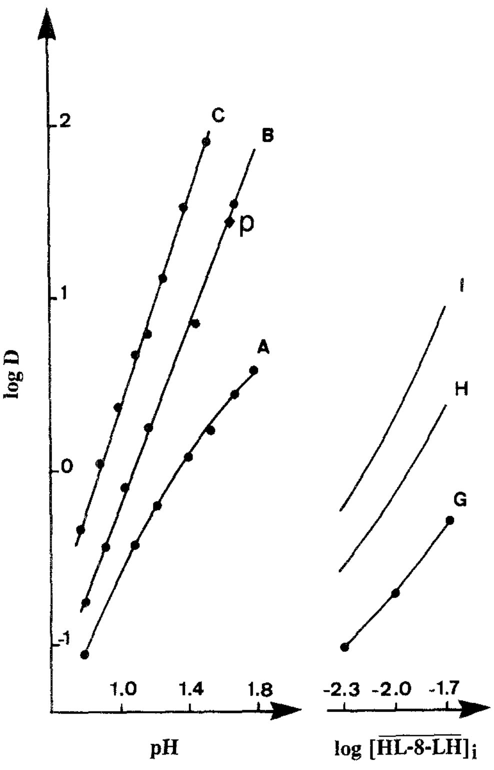

**Fig. 6.** Extraction of indium from 1 *M* perchlorate media with H*L*-8-*L*H and *TOPO* in chloroform: influence of the chelatant concentration. $[TOPO]_i$: $10^{-2} M$. $[\mathrm{H}L\text{-}8\text{-}L\mathrm{H}]_i$: $5 \cdot 10^{-3} M$ (*A*); $10^{-2} M$ (*B*); $2 \cdot 10^{-2} M$ (*C*). $pH = 0.8$ (*G*); 1.0 (*H*); 1.2 (*I*)

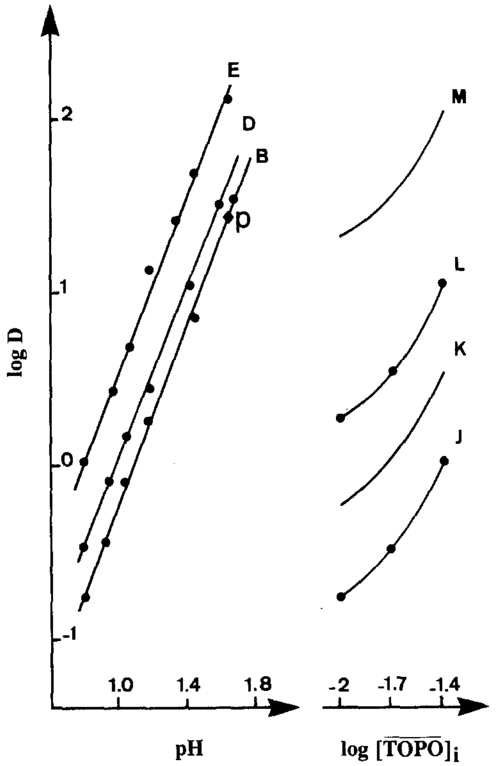

**Fig. 7.** Extraction of indium from 1 *M* perchlorate media with H*L*-8-*L*H and *TOPO* in chloroform: influence of the donor concentration. $[\mathrm{H}L\text{-}8\text{-}L\mathrm{H}]_i$: $10^{-2}\,M$. $[TOPO]_i$: $10^{-2}\,M$. (*B*); $2\cdot10^{-2}\,M$ (*D*); $4\cdot10^{-2}\,M$ (*E*). $pH=0.8$ (*J*); 1.0 (*K*); 1.2 (*L*); 1.6 (*M*)

centration of indium, therefore di- or polynuclear species are expected to occur in the organic phases.

The PMR spectrum of an organic extraction phase corresponding to the point "P" in the Fig. 6 and 7 (Table 1) shows that it is mainly composed of major species whose spectra are analogous to that of $\mathrm{In}_2(L\text{-}8\text{-}L)_3$, i.e. $\mathrm{In}_2(L\text{-}8\text{-}L)_3(TOPO)_n$. Minor species, approximately 8% of the "*L*" moieties, are attributed to polymeric species. In the IR spectra of the extraction phases, the coordination of *TOPO* upon indium includes a downshift of the ν (P=O) band from 1 139 cm$^{-1}$ (free *TOPO*) to ca. 1 100 cm$^{-1}$. This downshift is higher than that observed for the extractable species Zn(*L*-8-*L*)(*TOPO*), giving evidence for a stronger *M*−O bond.

Thus, the main extraction equilibrium may be written as:

$$2\,\mathrm{In}^{3+} + 3\,\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}} + \overline{n\,TOPO} \leftrightarrows \overline{\mathrm{In}_2(L\text{-}8\text{-}L)_3(TOPO)_n} + 6\,\mathrm{H}^+, \tag{17}$$

$$D_{23n} = 2[\overline{\mathrm{In}_2(L\text{-}8\text{-}L)_3(TOPO)_n}]/[\mathrm{In}^{3+}],$$

$$\log D_{23n} = \log K_{23n} + 6pH + n\log[\overline{TOPO}] + 3\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] + \log 2 + \log[\mathrm{In}^{3+}],$$

$$\log(D_{23n}/2[\mathrm{In}^{3+}]) = \log K_{23n} + 6pH + n\log[\overline{TOPO}] + 3\log[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}].$$

Taking into account that

$$[\overline{TOPO}] = [\overline{TOPO}]_i - n\,[\overline{\mathrm{In}_2(L\text{-}8\text{-}L)_3(TOPO)_n}] = [\overline{TOPO}]_i - (n/2)\,[\overline{\mathrm{In}}]$$

and that

$$[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}] = [\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i - 3\,[\overline{\mathrm{In}_2(L\text{-}8\text{-}L)_3(TOPO)_n}] = [\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]_i - (3/2)\,[\overline{\mathrm{In}}],$$

the curves $\log(\mathrm{D}/2[\mathrm{In}])$ vs. *pH*, vs. $[\overline{\mathrm{H}L\text{-}8\text{-}L\mathrm{H}}]$ and vs. $[\overline{\mathit{TOPO}}]$ have been drawn. Their slopes show that the major extraction species is indeed $\mathrm{In}_2(L\text{-}8\text{-}L)_3(\mathit{TOPO})_2$ and that species with a higher *TOPO*/In ratio also implied. $K_{232}$ was calculated from experimental data corresponding to low values of $[\overline{\mathit{TOPO}}]_i$: $\log K_{232} = 6.6 \pm 0.2$.

It is noticeable that the number of extracted indium species is much lower for the extraction with *TOPO* than for the extraction with H*L*-8-*L*H alone. This might be due to a preferential formation of $\mathrm{In}_2(L\text{-}8\text{-}L)_3(\mathit{TOPO})_n$ complexes from $\mathrm{In}_2(L\text{-}8\text{-}L)_3$, compared with that of $\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})(\mathit{TOPO})_m$ from $\mathrm{In}(L\text{-}8\text{-}L)(L\text{-}8\text{-}L\mathrm{H})$ or with that of $\mathrm{In}(L\text{-}8\text{-}L\mathrm{H})_3(\mathit{TOPO})_p$ from $\mathrm{In}(L\text{-}8\text{-}L\mathrm{H})_3$, in organic solution. Another possibility is that the extraction mechanism cannot be described by the classical scheme "extraction of metal by H*L*-8-*L*H alone, followed by an addition of *TOPO* upon the extracted complexes in organic solution". The $^{31}$P-NMR data of Table 2 clearly show that the interaction of $\mathrm{In}_2(L\text{-}8\text{-}L)_3$ with *TOPO* in $\mathrm{CHCl}_3$ ($\delta = 49.5$ ppm) is comparable to that of *TOPO* with $\mathrm{CHCl}_3$ ($\delta = 48.8$ ppm), although strong In – O=P bonds ($\delta = 68.5$ ppm) are formed during the synergistic extraction with H*L*-8-*L*H and *TOPO*. This clearly confirms the first assumption. Moreover, The PMR and $^{31}$P-NMR (Table 2) spectra of organic extraction phases with H*L*-8-*L*H alone, and where *TOPO* has been added after the separation of the phases, are also the sum of the spectra of their constituents.

Hence, the reaction path leading to the extracted complex $\mathrm{In}_2(L\text{-}8\text{-}L)_3(\mathit{TOPO})_2$ cannot consist in the reaction of *TOPO* in the organic phase with species extracted by H*L*-8-*L*H alone.

These results are analogous to those obtained for the synergistic extraction of indium with 4-acylpyrazol-5-ols and *TOPO* [7]. The chemical shifts of $^{31}$P are indeed quite similar in both cases (see Table 2) with an In – *TOPO* bond stronger than the Zn – *TOPO* bond of the extracted complex Zn(*L*-8-*L*)(*TOPO*).

**Table 2.** $^{31}$P Chemical shifts of *TOPO* ($\delta$: ppm/$\mathrm{H_3PO_4}$)

| | Solvent | $\delta$: ppm | Comments | Ref. |
|---|---|---|---|---|
| *TOPO* | Toluene | 39.9 | No interaction | [7] |
| *TOPO* + H*PMBP* (1 : 1) | id. | 49.7 | P=O – H bonds (weak) | [7] |
| *TOPO* + $\mathrm{In}(\mathit{PMBP})_3$ (1 : 1) | id. | 53.0 | P=O – In weak bonds | [7] |
| Loaded extraction phases<br>In/H*PMBP* + *TOPO* | id. | 50.7<br>65.7 | P=O – In weak bonds<br>P=O – In strong bonds | [7] |
| *TOPO* | $\mathrm{CHCl}_3$ | 48.8 | P=O – H bonds | This work |
| H*L*-8-*L*H + *TOPO* (1 : 1) | id. | 48.8 | Weak bonds:<br>*TOPO* – H*L*-8-*L*H<br>*TOPO* – $\mathrm{In}_2(L\text{-}8\text{-}L)_3$<br>and/or *TOPO* – $\mathrm{CHCl}_3$ | This work |
| $\mathrm{In}_2(L\text{-}8\text{-}L)_3$ + *TOPO* (1 : 1) | id. | 49.5 | | This work |
| Loaded extraction phase<br>(In/H*L*-8-*L*H) + added *TOPO* | id. | 49.0 | | This work |
| Loaded extraction phase<br>In/H*L*-8-*L*H + *TOPO* | id. | 49.6<br>68.5 | <br>P=O – In strong bonds | This work |
| Zn(*L*-8-*L*)(*TOPO*) | id. | 59.0 | P=O – Zn medium bonds | [5] |

## Conclusion

The typical feature of the above systems is obviously the complexity of the extraction processes, especially when the acidic extractant is used alone: at least five species, likely more, are present in the organic phases. The major ones are In(*L*-8-*L*)(*L*-8-*L*H), $In_2$(*L*-8-*L*)$_3$ and In(*L*-8-*L*H)$_3$ at low *pH*, and di- or polynuclear ones at high *pH*. The presence of synergistic tri-*n*-octylphosphine oxide drastically simplifies the extraction process, which is described by the extraction of one major species $In_2$(*L*-8-*L*)$_3$(*TOPO*)$_2$ and of some minor species (ca. 8%). Like in the extraction of indium by the parent compound 1-phenyl-3-methyl-4-benzoylpyrazol-5-ol (H*PMBP*, see Fig. 1), the addition of *TOPO* upon indium chelate(s) in the organic phase cannot describe the extraction mechanism.

For equal concentrations of "*L*H" chelatant groups, indium is slightly better extracted with H*L*-8-*L*H alone than with H*PMBP* alone ($\Delta pH_{1/2} = 0.12$). This is no longer valid for the synergistic extractions ($\Delta pH_{1/2} = -0.2$), which might be due to a high lipophilicity of the extracted complex In(*PMBP*)$_3$(*TOPO*)$_2$, with two *TOPO* units per In atom, compared with $In_2$(*L*-8-*L*)$_3$(*TOPO*)$_2$.

In this work, NMR throws light on both thermodynamic and mechanistic aspects of the extraction and gives information upon the stereochemistry of extracted species. Thus, it appears as a particularly useful tool complementary to analytical techniques in liquid-liquid extraction studies.

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