

## *lel<sub>2</sub>ob* and *ob<sub>2</sub>lel* Cage Complexes Based on [Co(pn)<sub>3</sub>]<sup>3+</sup> (pn = Propane-1,2-diamine): Synthesis, Resolution, and Tentative Identity of Their *Fac* and *Mer* Geometrical Isomers

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Encapsulation of [Co(*R/S*-pn)<sub>3</sub>]<sup>3+</sup> affords the cobalt(III) sarcophagine(sar)-type complexes with stabilized diamine chelate ring conformations; we describe the synthesis, resolution and tentative identity of the one *fac* and three *mer* geometrical isomers of the *lel<sub>2</sub>ob* cages, as well as the subsequent conversion to their *ob<sub>2</sub>lel* diastereoisomers.

The ambiguity introduced by the conformational flexibility of the [M(X)<sub>2</sub>-sar]<sup>n+</sup> complexes (Figure 1; X = apical cap substituents, sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]eicosane)<sup>1</sup> necessitates formation of cage complexes with stabilized diamine chelate ring conformations.<sup>2,3</sup> [Co(*R/S*-pn)<sub>3</sub>]<sup>3+</sup> (pn = propane-1,2-diamine) provides a unique series of twelve enantiomeric pairs (Δ and Λ) of diastereoisomers with parallel and oblique conformational variations (*lel<sub>3</sub>*, *lel<sub>2</sub>ob*, *ob<sub>2</sub>lel*, and *ob<sub>3</sub>*),<sup>4</sup> by virtue of the pn methyl substituent favouring an equatorial orientation on the five-membered chelate rings.<sup>5</sup> A statistical distribution results in three *meridional* and one *facial* geometrical isomers for each of the conformational variants.<sup>6,7</sup> These *mer* isomers are degenerate for (pseudo-) C<sub>3</sub> symmetry, which provides a statistical predominance of 3 *mer* : 1 *fac* in the *lel<sub>3</sub>* and *ob<sub>3</sub>* systems.

Recently, one of us synthesised and resolved the *lel<sub>3</sub>*- and *ob<sub>3</sub>*-[Co(NH<sub>2</sub>)<sub>2</sub>-pnsar]<sup>3+</sup> cage diastereoisomers (Figure 2;

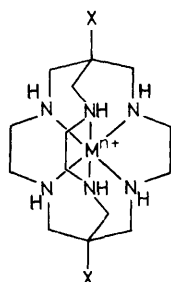


Figure 1. [M(X)<sub>2</sub>-sar]<sup>n+</sup> complex.

*fac*-pnsar = 1,8-diamino-4,12,17-trimethylsar; *mer*-pnsar = 1,8-diamino-4,11,17-trimethylsar).<sup>8,9</sup> The *lel<sub>3</sub>* cage isomers have surprisingly different characteristics compared to those of their *ob<sub>3</sub>* diastereoisomers, but their respective geometrical *fac* and *mer* isomers have virtually identical properties.<sup>8</sup> We now report the syntheses of the *lel<sub>3</sub>*, *lel<sub>2</sub>ob*, and *ob<sub>2</sub>lel* cage complexes in a one-pot reaction from an equilibrium mixture of [Co(*R/S*-pn)<sub>3</sub>]<sup>3+</sup> substrate (*lel<sub>3</sub>* = 36%, *lel<sub>2</sub>ob* = 42%, *ob<sub>2</sub>lel* = 18% and *ob<sub>3</sub>* = 4%)<sup>7</sup> using formaldehyde/nitromethane under basic conditions,<sup>1</sup> to give a mixture of the [Co(NO<sub>2</sub>)<sub>2</sub>-pnsar]<sup>3+</sup> diastereoisomers. After reducing the cap nitro

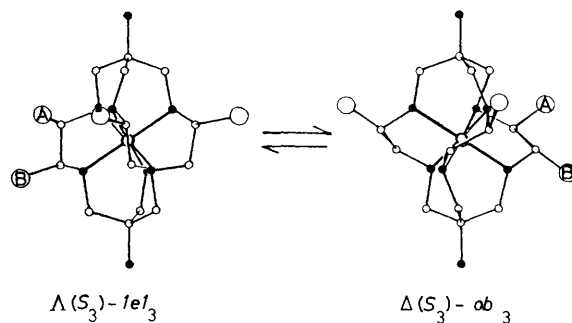
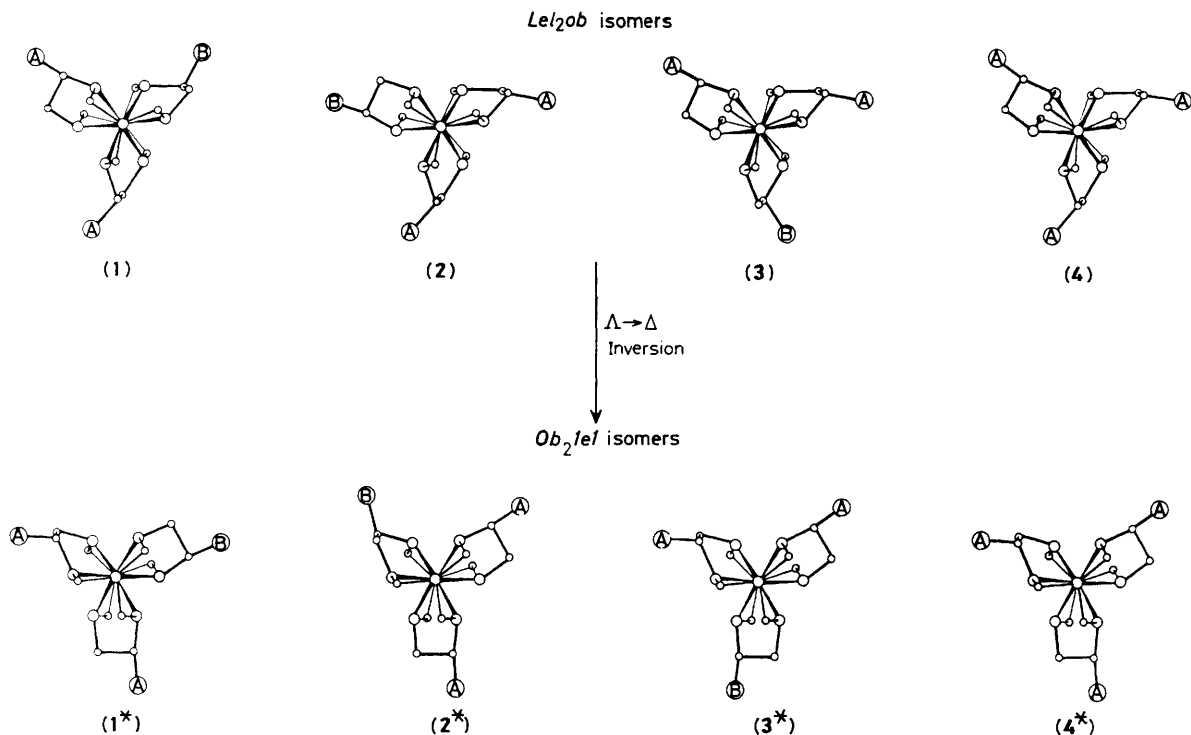


Figure 2. Interconversion of *lel<sub>3</sub>*- and *ob<sub>3</sub>*-[Co(NH<sub>2</sub>)<sub>2</sub>-pnsar]<sup>3+</sup> complexes. *Fac* when A = methyl above and B = H below; *Mer* when B = methyl below, A = H above (H atoms are excluded for clarity and ● = N).



**Scheme 1.** Top view of the conversion of  $\Lambda(S_2R)$ -*lel<sub>2</sub>ob* isomers to their  $\Delta(S_2R)$ -*ob<sub>2</sub>lel* diastereoisomers. A = methyl above, B = methyl below.

substituents to amines with Zn/HCl,<sup>1</sup> the isomer mixture was initially resolved on an SP Sephadex C-25 cation exchange column using 0.20 M  $K_2SO_4$  eluent; two major front orange bands and one minor back orange band were isolated. The two major bands were further resolved on a one-metre SP Sephadex C-25 column using 0.25 M  $Na_3PO_4$  eluent. The first band (~23% yield) was resolved into two products and identified by  $^{13}C$  n.m.r. as the *mer* and *fac* isomers of the *lel<sub>3</sub>*-[Co(NH<sub>2</sub>)<sub>2</sub>-pn<sub>3</sub>ar]<sup>3+</sup> cation.<sup>8</sup> The second band (~11% yield) was similarly resolved into four products by continuous recycling on the column. These have been identified as the one *fac* and three *mer lel<sub>2</sub>ob* isomers, indicative from their composite  $^{13}C$  spectral features of the pure *lel<sub>3</sub>* and *ob<sub>3</sub>* cages. The four very similar *lel<sub>2</sub>ob*  $^{13}C$  spectra each show the expected 17 carbon atoms.† The lower yield of the *lel<sub>2</sub>ob* cage is due to the increased *ob* character of the starting substrate. This rationale follows from the fact that *lel<sub>3</sub>*-[Co(pn)<sub>3</sub>]<sup>3+</sup> encapsulates with ~70% success while the *ob<sub>3</sub>* substrate fails to form a cage.<sup>8</sup>

The tentative identification of these *lel<sub>2</sub>ob* isomers has been rationalized by their elution order relative to the elution behaviour of the *lel<sub>3</sub>* and *ob<sub>3</sub>* cages. The *lel<sub>3</sub>* cages elute well ahead of their *ob<sub>3</sub>* diastereoisomers,<sup>8</sup> indicative of the more open pseudo-*C<sub>2</sub>* *lel* faces which have the protons on the co-ordinated amines better disposed for hydrogen-bonding with counter-ions. Furthermore, in both *lel<sub>3</sub>* and *ob<sub>3</sub>* cases the *mer* isomers elute marginally faster than their *fac* partners, indicative of the more accessible faces that eventuate in the respective *mer* situations. Hence the slowest moving *lel<sub>2</sub>ob*

isomer (4) must be *fac* (Scheme 1). The fastest moving isomer (1) must have the open *mer-lel<sub>2</sub>* face, while isomer (3), with the closed *mer-lel<sub>2</sub>* face, eluted more slowly. Isomer (2), with the *fac-lel<sub>2</sub>* face, co-eluted with (1) for five cycles on the column before a separation became obvious. This identification is further corroborated by the unequal amounts of the *lel<sub>2</sub>ob* cage isomers that were formed, despite the probability that the *lel<sub>2</sub>ob*-[Co(pn)<sub>3</sub>]<sup>3+</sup> substrate isomers form in approximately equal amounts under equilibrium conditions.<sup>7</sup> The yields indicate a pattern of reactivity which is a function of the *lel* and *ob* character of the initial substrate as well as the steric influence of the pn methyl substituents. The *fac-lel<sub>2</sub>ob* isomer (4), with the one trigonal N<sub>3</sub> face crowded by one *ob* and two *lel* methyl substituents, gave the lowest relative yield (~5%). Transposing the *ob* methyl to the opposite trigonal N<sub>3</sub> face, producing the *mer* isomer (2) with both the top and bottom faces least hindered, gave the highest relative yield (~43%). The other two intermediate cases, where the *ob* methyl shares an N<sub>3</sub> trigonal face with one of the *lel* methyl substituents, gave intermediate relative yields of isomers (1) (~24%) and (3) (~28%).

The  $^{13}C$  n.m.r. spectrum of the third minor band (<1% yield) from the initial reaction indicated that it is mainly a single isomer of *ob<sub>2</sub>lel* cage which has the required composite spectral features of the *ob<sub>3</sub>* and *lel<sub>3</sub>* diastereoisomers.† This drastic decrease in capping ability is due to the increased *ob* character of the substrate and an alternative strategy was adopted to synthesise and identify the *ob<sub>2</sub>lel* cage isomers. This involved the same procedure developed for the synthesis of the *ob<sub>3</sub>* cages.<sup>8</sup> As the *ob<sub>3</sub>* substrates did not encapsulate, the *ob<sub>3</sub>* cages were eventually synthesised by removing Co<sup>II</sup> from the *lel<sub>3</sub>* cage complexes in concentrated NaCN and then reinserting a labile form of Co<sup>III</sup> into the free cage ligand, via *trans*-[Co(py)<sub>4</sub>Cl<sub>2</sub>]Cl (py = pyridine) in 2-methoxyethanol, effectively isomerizing, for example, the  $\Lambda(S_3)$ -*lel<sub>3</sub>* cage to its  $\Delta(S_3)$ -*ob<sub>3</sub>* diastereoisomer (Figure 2). We performed this

†  $^{13}C$  N.m.r. signals, assigned by APT and DEPT, occur in the following ranges (D<sub>2</sub>O with external reference dioxane =  $\delta$  67.3): pn-CH<sub>3</sub>, *lel* =  $\delta$  13.6–14.4, *ob* =  $\delta$  12.4–12.7; pn-CH<sub>2</sub>, *lel* =  $\delta$  60.7–61.9, *ob* =  $\delta$  55.2–57.2; pn-CH, *lel* =  $\delta$  63.8–65.2, *ob* =  $\delta$  57.4–59.3; Cap-CH<sub>2</sub>,  $\delta$  45.2 (adjacent to *ob* pn-CH<sub>3</sub>) to 54.7; Cap quaternary C, 55.6–58.2.

interconversion on the three *mer* isomers of the *lel<sub>2</sub>ob* cages, in effect transforming, for example, the  $\Lambda(S_2,R)$ -*lel<sub>2</sub>ob* cages to their  $\Delta(S_2,R)$ -*ob<sub>2</sub>lel* diastereoisomers in overall conversions of ~10% (Scheme 1). The conversion product from *lel<sub>2</sub>ob* (**1**) has the same <sup>13</sup>C n.m.r. spectrum as that of the *ob<sub>2</sub>lel* cage (**1\***) isolated from the original one-pot template synthesis, which is consistent with the reactivity discussed above.

A surprising feature of this cage system occurs in the visible spectral regions. The first visible transition, of  $^1A_{1g} \rightarrow ^1T_{1g}$  origin, occurs at 476 nm ( $\epsilon \sim 150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for the *lel<sub>3</sub>*-[Co(NH<sub>2</sub>)<sub>2</sub>-pnsar]<sup>3+</sup> cages and at 450 nm ( $\epsilon \sim 85 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for the *ob<sub>3</sub>* cages. Although one might expect the *lel<sub>2</sub>ob* and the *ob<sub>2</sub>lel* cages to have transitions at intermediate wavelengths, the *lel<sub>2</sub>ob* transition occurs at 484 nm ( $\epsilon \sim 160 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and the *ob<sub>2</sub>lel* at 475 nm ( $\epsilon \sim 200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), both close to the *lel<sub>3</sub>* values. The respective *fac/mer* isomerism has minimal effect on these visible transitions. Molecular mechanics calculations show that the *ob<sub>3</sub>* cages have close to octahedral CoN<sub>6</sub> core symmetry and the shortest Co-N bond lengths,<sup>8</sup> and this reflects in the lower extinction coefficient and shorter wavelength. The *lel<sub>3</sub>* cages undergo some trigonal twist (the twist angle,<sup>10</sup>  $\phi \sim 56^\circ$ ) imparting C<sub>3</sub> symmetry to the CoN<sub>6</sub> chromophore. The rise in extinction coefficients for the *lel<sub>2</sub>ob* and *ob<sub>2</sub>lel* cage isomers reflect a further loss of CoN<sub>6</sub> inner co-ordination-sphere symmetry.

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