Seven-Coordinate d^0 and d^{10} Ions − Computational and Experimental Studies on Tris(tropolonato)metal(III)−TOPO Adducts

Jerzy Narbutt,*[a] Marian Czerwiński,[b] and Jadwiga Krejzler[a]

Keywords: Chelates / Thallium / Yttrium / Coordination chemistry / Density-functional calculations / Hypervalent compounds

The stabilities of molecular adducts between tris(tropolonato)metal(III) chelates of some tripositive ions of Groups 3 and 13 and trioctylphosphane oxide (TOPO) were studied using both theoretical and experimental methods. Density-functional calculations were used to optimise the structure and characterise tris(tropolonates) of scandium and yttrium, a series of model chelates of gallium, indium, thallium, scandium, and yttrium, as well as the 1:1 adducts of these chelates with trimethylphosphane oxide. The calculated energy of adduct formation decreased in the order: Y > Sc > Tl > In. Stability constants of the 1:1 (and some 1:2) TOPO adducts in solution, determined by synergistic solvent extraction of metal tropolonates, decreased in the same order. Both methods show that gallium does not increase its coordination number (CN) above six. The chelates of d^{10} ions (CN 6) and their adducts (CN 7) are less stable than the corresponding d^0 species, because the former are hypervalent compounds with no higher-lying metal *n*d orbitals participating in bonding, while the latter have easily accessible vacant $(n-1)$d orbitals. A significant distortion of the chelate structure makes the adducts of smaller ions less stable. Examination of bonding molecular orbitals in the adducts shows an unusual origin of the metal–TOPO bond, which may be due to a contribution from π-bonding. Differences in some characteristics of indium and thallium compounds can be explained by relativistic properties of thallium.

Introduction

Metal ions with high coordination numbers (CN) continue to attract interest,[1,2] and the reason is not purely academic. The ability of a metal ion in a complex to increase its CN makes it possible to form inner-sphere adducts, to exchange ligands by an associative mechanism, to affect catalytic properties of the compound, etc. Inner-sphere solvation of metal complexes influences their behaviour in solution, which is of importance in different fields such as e.g. metal ion controlled biological processes and processes of separation of metal ions.

The coordination stereochemistry of metal complexes depends on the relations between geometrical and electrostatic factors on one side, and the electronic configuration of the metal ions on the other.[3] Geometrical models consider not only the size of the metal ion and ligand atoms, but also the ligand structure.[3,4] For example, the bite in rigid bidentate ligands and the intraligand strain affect the coordination environment of the ion.[3,5,6] Electrostatic metal−ligand attraction and ligand−ligand repulsion in the coordination polyhedron, which depend on the charges on the ion and on the ligand atoms, also affect the geometry of the complex and the strength of metal−ligand bonds. Generally, the weaker and longer the bonds, i.e. the easier the deformation of the coordination polyhedron, the greater the tendency to increase the CN by coordination of (an) additional ligand(s).[7] For less stable metal chelates, the role of ligand structure, in particular of bite size, is less pronounced.[6] The electronic configuration of the metal ion is also important in this connection. The effect of d-orbital population in transition metal ions on their CN was recently discussed in terms of the angular overlap model.[2]

The major objective of this work was to explain how the tendency to increase CN of a central metal ion in neutral chelates with bidentate ligands is influenced by properties of the ion, in particular its radius and electron configuration. Particularly interesting in this respect was the comparison of d^{10} and d^0 ions whose $(n-1)$d orbitals were either completely filled or vacant. We expected that d^0 ions with $(n-1)$d orbitals easily accessible for hybridisation would attain CN = 7 more readily than d^{10} ions with distant vacant *n*d orbitals.[8]

The metal ions selected were trivalent gallium, indium, and thallium from Group 13, as well as scandium and yttrium from Group 3. The tropolonate anion, $C_7H_5O_2^-$ − a short-bite bidentate ligand − made it possible for the ions to reach CN > 6.[6] Trioctylphosphane oxide (TOPO) − a very strong electron donor − was an auxiliary neutral monodentate ligand. Practical interest in studying such systems stemmed from the application of indium tropolonates and other α-diketonates for labelling blood cells with radioindium to be used in nuclear medicine,[9] while gallium tro-

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[a] Department of Radiochemistry, Institute of Nuclear Chemistry and Technology,
Dorodna 16, 03195 Warsaw, Poland
Fax: (internat.) + 48-22/8111-532
E-mail: jnarbut@orange.ichtj.waw.pl
[b] Chemistry Institute, Pedagogical University,
Al. Armii Krajowej 13/15, 42201 Czestochowa, Poland
E-mail: czerwinski@ichn.ch.pwr.wroc.pl

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polonate was not effective in this respect.[10] Other reasons for our interest were relativistic properties of thallium and scarcity of data on its mixed-ligand complexes.[1,11,12]

Both quantum chemistry calculations and an experimental technique were used in our studies. Theoretical calculations based on Density-Functional Theory (DFT), particularly suitable for studying metal complexes,[13] were carried out for the chelates and adducts. We obtained information on their structure, energy and charge distribution, and verified our hypothesis on the role of electronic configuration of the ion. The calculated (DFT) energies of adduct formation correlate well with the experimental stability constants of the metal tropolonate − TOPO adducts in solution, determined by solvent extraction, and considered as a measure of the tendency of a metal ion to increase its CN over six.

Computational Details

Density-functional calculations were carried out both on the metal(III) tris(chelates) (CN = 6) and on their 1:1 adducts (CN = 7). To save computer resources, only two tris(tropolonato)metal(III) structures were optimised, and then the whole system was modelled. In order to reproduce symmetry of chelate rings in tris(chelato)metal(III) complexes, as well as their quasi-aromatic character (in the original complex they are coupled with the seven-membered ring of tropolone) the simple bidentate anionic ligand $O-CH=CH-O^-$ (denoted as αdik)[14] was selected as a model for tropolonate, while trimethylphosphane oxide (denoted as TMPO or B) replaced TOPO. Additionally, to check the reliability of the model with the radical anionic ligand another system was studied consisting of Sc and Y chelates (and their TMPO adducts) with a molecular ligand, $O=CH-CH_2-O^-$. All the calculations were based on the DFT method as implemented in the GAUSSIAN-94 program.[15] The Lanl2dz double-ζ basis set,[16] Becke three-parameter functional (B3LYP),[17] and Berny geometry-optimisation algorithm[18] were used. The charge density was obtained from Mulliken overlap and bonding population analysis.[19] The calculations were performed by using relativistic effective core potential, which retained the outer shells (e.g. $5d^{10}6s^{2}6p^{1}$ shells of the Tl atom) in the valence space, replacing the rest of electrons by relativistic effective potentials. The basis sets for the metals were supplemented with polarisation functions taken from Andzelm et al.[20]

CAS SCF Calculations

In order to evaluate the tendency of the d^0 and d^{10} ions to reach a valence state corresponding to CN = 7, we carried out multi-configurational self-consistent-field calculations with the complete active space self-consistent-field (CAS SCF)[21] approach. Promotion energies, defined as differences between the calculated energies of the ground and excited states, were calculated for single isolated atoms. The active space with seven electrons distributed over eight orbitals was taken for the CAS SCF calculations; this led to 2352 configuration states. The calculations were carried out for the ground state and the two lowest excited states of the atoms, of total multiplicity two. All the numerical calculations were carried out using supercomputers: Cray T3E, Cray J90, and Cray Y-MP.

Results

Geometry Optimisation and Charge Distribution

Firstly the optimisations of geometry of the chelates $[ML_3]$ (where L = trop or αdik; Table 1), of a free TMPO molecule, and of their adducts $[ML_3 \cdot TMPO]$ (Table 2) were performed. The coordination polyhedra of the chelates were D_3-twisted trigonal antiprisms (Figure 1a).

Optimisation of systems consisting of $[ML_3]$ and TMPO, starting with the previously optimised structures, resulted in stable $[ML_3 \cdot TMPO]$ adducts with CN = 7, of significantly distorted structures for Sc, Y, In, and Tl^{III} ions (Figure 1b). The smallest Ga^{III} ion preserved a CN = 6 in the adduct by breaking one of the six $Ga-O^L$ bonds (Table 2).

Formation of the $M-O^B$ bond was accompanied by a charge (electron density) transfer from TMPO to $[ML_3]$. Its magnitude is given by the Δq value (Table 2), which is equal to the total charge on each of the two components in the

Table 1. Optimised geometry of the chelates $[M(trop)_3]$ and $[M(\alpha dik)_3]$, charge distribution on their atoms and Mulliken bond population (GAUSSIAN 94 with potential B3LYP in the basis Lanl2dz)

	Calculated geometry[a] and charge distribution						Literature data[b]			
	M−O	$O-O_{bite}$	OMO	q_M	q_{OL}	q_{M-OL}	M−O	$O-O_{bite}$	OMO	r_i [c]
$Sc(trop)_3$	210.9	251.5	73.2	1.227	−0.490	0.156	210	252	74	74.5
$Sc(\alpha dik)_3$	213.3	258.9	74.8	1.270	−0.422	0.155				
$Y(trop)_3$	228.1	255.2	68.0	1.347	−0.501	0.147	−	−	−	90
$Y(\alpha dik)_3$	230.9	264.3	69.8	1.404	−0.430	0.160				
$Ga(\alpha dik)_3$	198.9	260.5	81.8	1.205	−0.410	−	196.7	255.8	81.1	62.0
$In(\alpha dik)_3$	213.4	266.4	77.2	1.448	−0.446	0.177	213.4	260.7	75.3	80.0
$Tl(\alpha dik)_3$	231.7	277.9	73.7	1.353	−0.407	0.134	−	−	−	88.5

[a] Distances in pm; the C−O and C−C distances in each $[M(trop)_3]$ and $[M(\alpha dik)_3]$ are equal to 131.8(1) and 149.1(2), and to 131.7(1) and 142.9(1) pm, respectively; the bite angle, OMO, in deg. [b] Distances [pm] and bite angles [deg] for crystalline tropolonates; ref.[22] [c] Shannon ionic radii for six coordination [pm]; ref.[23]

Table 2. Optimised geometry of the $[ML_3\cdot TMPO]$ adducts, charge distribution on their atoms and Mulliken bond population (GAUSSIAN 94 with potential B3LYP in the basis Lanl2dz)

	Calculated geometry and charge distribution in the adducts[a]									
	Range $M-O^L$	$M-O^B$	MOP	q_M	q_{O^L}[b]	q_{O^B}	Δq[c]	q_{M-O^L}[b]	q_{M-O^B}	$q_{P=O}$[d]
$Sc(trop)_3\cdot B$	211.8−227.8	208.0	136.7	1.209	−0.466	−0.795	0.203	−	−	−
$Sc(\alpha dik)_3\cdot B$	213.7−231.5	206.7	138.7	1.245	−0.401	−0.803	0.220	0.159	0.136	0.291
$Y(trop)_3\cdot B$	230.5−241.5	225.4	136.3	1.340	−0.484	−0.795	0.195	−	−	−
$Y(\alpha dik)_3\cdot B$	232.2−244.8	222.7	139.9	1.342	−0.414	−0.802	0.210	0.154	0.140	0.298
$Ga(\alpha dik)_3\cdot B$	190.3−302.3[e]	189.7	−	−	−	−	−	−	−	−
$In(\alpha dik)_3\cdot B$	214.0−241.8	204.6	137.4	1.484	−0.428	−0.855	0.185	0.150	0.160	0.276
$Tl(\alpha dik)_3\cdot B$	234.6−244.3	226.1	132.5	1.383	−0.403	−0.808	0.184	0.119	0.117	0.306

[a] Distances, angles and charges as in Table 1. [b] The average values for six O^L atoms and/or six $M-O^L$ bonds; for the actual values see Supporting Information; [c] The total charge-transfer from TMPO to chelate. [d] $q_{P=O} = 0.494$ in free TMPO molecule. [e]] Broken Ga−O bond; open chelate ring.

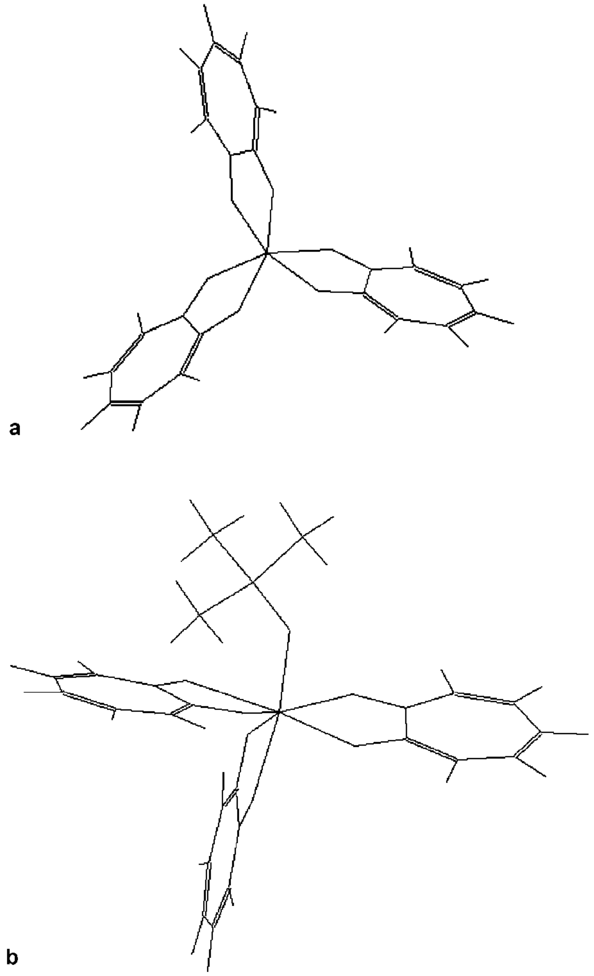

Figure 1. Stick models of the optimised structures: (a) $[Sc(trop)_3]$ chelate; (b) $[Sc(trop)_3\cdot TMPO]$ adduct

adduct. The dipole moments of the adducts were much greater than that of TMPO alone, and the TMPO molecule in the adduct was strongly polarised. In the Supporting Information the computed coordinates and total charges of all atoms in the Sc, Y, (Ga), In, and Tl^{III} chelates and adducts studied, the dipole moments, and other data are reported.

Energy Calculations

Energies of Chelate Formation and Adduct Formation and Their Components

The respective ΔE_{ch} and ΔE_{ad} values were calculated after full optimisation of all the components, and computing their total energies with the same Lanl2dz basis set. The use of polarisation functions had little effect on the results of the calculations (Table 3, footnote c).

The bond analysis developed by Ziegler and Rauk[24] made possible an insight into the character of metal−ligand interactions in the complexes studied. The energy of adduct formation could be separated into contributions related to the energy of structure distortion, ΔE_d, for both components of the adduct, and the energy of interaction, ΔE_{int}, between the distorted components. In our system, $\Delta E_{d,ch}$ reflects significant changes in the chelate structure upon adduct formation, involving rearrangement of the first coordination sphere of the metal ion, and $\Delta E_{d,B}$ − a slight deformation of the TMPO structure when in the adduct. Further separation of the ΔE_{int} term is also possible into orbital interaction energies (charge transfer) and steric interactions (Pauli repulsion and Coulomb electrostatic terms), the former being the main stabilising factor in some adducts [Equation (1)].[25]

$$\Delta E_{ad} = \Delta E_{d,ch} + \Delta E_{d,B} + \Delta E_{int} \tag{1}$$

The values $\Delta E_{d,ch}$ and $\Delta E_{d,B}$ were calculated (Table 3) as the differences between the total bond energies of the $[M(\alpha dik)_3]$ (and TMPO) molecules in their distorted and optimised structures.[26] The ΔE_{int} values were obtained with the use of Equation (1). However, because these values might be in error due to calculating their components with the use of different basis sets, we independently calculated another set of $\Delta E_{int}'$ values, equal to the differences between the total energies of the adduct and of its subunits −

Table 3. Calculated (GAUSSIAN 94 with potential B3LYP in the basis Lanl2dz) formation energies of chelates and adducts [M(αdik)$_3$·TMPO], distortion energies of the chelates and TMPO, and the energy of interaction between the components of the adducts

Chelate	ΔE_{ch}	ΔE_{ad} [a]	$\Delta E_{d,ch}$	$\Delta E_{d,B}$	ΔE_{int}	$\Delta E_{int}'$	E^{σ} [b]	E^{π} [c]
	Formation energies and their components [kJ mol^{-1}]						Orbital energies [a.u.][d]	
Sc(trop)$_3$		−87.5						
Sc(αdik)$_3$	−2328	−95.5	81.0	7.0	−183	−188	−0.4099	−0.2936
Y(trop)$_3$		−93.0						
Y(αdik)$_3$	−1077	−120	59.0	7.0	−186	−183	−0.4135	−0.2943
Ga(αdik)$_3$	−657	[−42][e]	–	–	–	–	–	–
In(αdik)$_3$	−639	−74.2	114	7.7	−196	−196	−0.4132	−0.2904
Tl(αdik)$_3$	−353	−82.6	54.5	7.0	−144	–	−0.4129	−0.2897

[a] The respective ΔE_{ad} values calculated using one (and two) polarisation function(s) are equal to: −70 kJ mol^{-1} for In; −80 kJ mol^{-1} for Tl; −98 (−99) kJ mol^{-1} for Sc; and −123 (−122) kJ mol^{-1} for Y. [b] Energies of bonding molecular orbitals in the adducts; σ-type bonds; the average energies for α and β spins. [c] π-type bonds; the average energies for α and β spins and for five different MOs, including the indium adduct. [d] 1 a.u. = 2262 kJ mol^{-1}. [e] Broken Ga−O bond; open chelate ring.

chelate and TMPO − all in the same structure, optimised for the adduct.[27] The results, except for thallium where the procedure was not convergent, are presented in Table 3. The reasonable agreement between both sets of data makes the ΔE_{int} values convincing.

Promotion Energies

Data were calculated for the metal atoms by using the CAS SCF method. The ground and excited states of each atom are well represented by single determinants (the coefficients of the SCF configurations being greater than 0.8). The ground state was characterised by the $s^2p^3d^2$ configuration, the excited states by $s^2p^2d^3$. High values of ca 330 kJ mol^{-1}, corresponding to the transfer of one electron from the ground-state p orbital to the lowest excited-state d orbital, were obtained for isolated atoms of In and Tl. In contrast, the respective values for the Group 3 atoms were either much lower (ca 100 kJ mol^{-1} for Sc), or even negative (−5 kJ mol^{-1} for Y). In our opinion, the difference between the above data obtained for the d- and p-block metal atoms well characterises the change CN = 6 → CN = 7, which relates to the formation of the 1:1 TOPO adducts by the respective chelates.

Molecular Orbitals

In order to characterise the [ML$_3$]−TMPO bonds by the electron density localised in the bond region, i.e. between the O^B and M atoms (q_{M-O^B} Table 2), the population and the energy of all occupied molecular orbitals (MO) in the adducts were calculated after full optimisation of the structures. To find the original MOs of [M(αdik)$_3$] and TMPO, which contribute to formation of the adduct bond, the respective data including some vacant MOs were also calculated for TMPO and the chelates. All the calculated MOs of the chelates and TMPO (Supporting Information), and of the adducts (Figure 2) were examined with the use of MOLDEN,[28] a program for visualisation. Tables 1 and 2 show M−O bond populations in the chelates and adducts, respectively, and Table 3 shows the average energies of bonding MOs (σ and π) in the adducts.

Solvent Extraction Studies

Solvent extraction is a technique particularly useful for characterising molecular adducts formed in solution by amphiphilic neutral metal chelates and neutral hydrophobic ligands, e.g. TOPO.[6] If a metal ion, M^{m+}, and a bidentate organic ligand in the anionic form, L$^-$, in aqueous solution combine, the neutral chelate formed, ML$_m$, may then be transferred to an immiscible organic phase on bringing the solutions into contact. The equilibrium can be described by an extraction constant, where square brackets denote the molar concentrations[29] of the given species, and subscripts "org" and "aq" refer to the organic and aqueous phase, respectively [Equation (2)].

$$K_{ex} = \frac{[ML_m]_{org}[H^+]^m_{aq}}{[M^{m+}]_{aq}[HL]^m_{org}} \qquad (2)$$

The transfer can be enhanced by formation (in the organic phase; the subscripts omitted) of molecular adducts [ML$_m$·iB] where B denotes an auxiliary neutral hydrophobic ligand, e.g. TOPO [Equation (3)].

$$ML_m + iB \rightleftarrows ML_m{\cdot}iB \qquad (3)$$

The stability constants, $\beta_{m,i}$, of the adducts, equal to the equilibrium constants of reactions (3), are expressed in terms of molar concentrations, assuming the solution to be ideal associated. This assumption is reasonable in view of trace concentration of the chelate. The distribution ratio of the metal is given by Equation (4).

$$D = \frac{[ML_m]_{org} + \sum_i [ML_m \cdot iB]_{org}}{[M^{m+}]_{aq} + \sum_j [ML_j^{m-j}]_{aq}} \qquad (4)$$

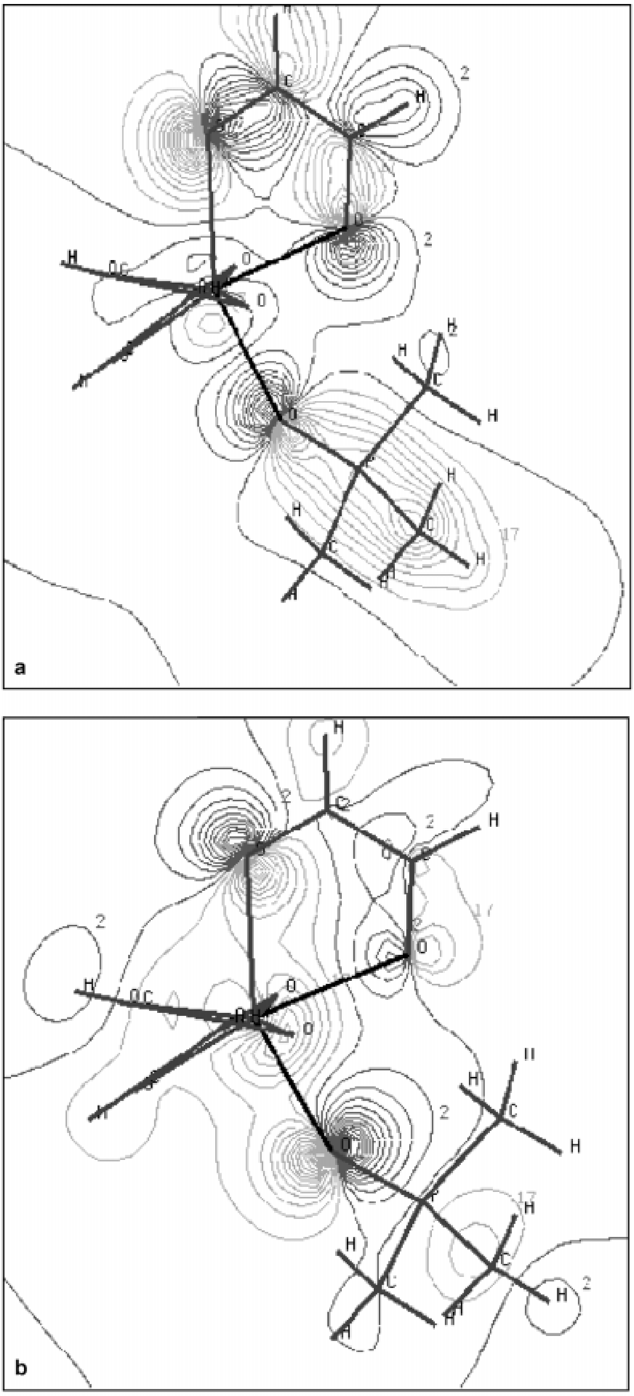

Figure 2. 3D contours of selected bonding molecular orbitals in the [Y(αdik)$_3$·TMPO] adduct: (a) σ symmetry, $E = -0.4006$ a.u.; (b) π symmetry, $E = -0.2874$ a.u.

In the case of two adducts $ML_m{\cdot}B$ and $ML_m{\cdot}2B$ predominating in the organic phase Equation (4) can be rearranged to Equation (5), where D_0 denotes the distribution ratio in the absence of TOPO in the system, and [B] − the molar concentration of free TOPO in the organic phase at equilibrium.

$$\frac{D}{D_0} = 1 + \beta_{m,1}[B] + \beta_{m,2}[B]^2 \qquad (5)$$

Only in the case of gallium, which is extracted from HCl solutions as solvates, Ga(TOPO)$_n$Cl$_3$, D_0 denotes the distribution ratio at the same TOPO concentration, but in the absence of tropolone in the system. In the cases when D was independent of pH and of the concentration of HL (plateau region, when the only form of the metal in the aqueous phase was the uncharged chelate, ML_m), D_0 was equal to partition constant, P, defined as the ratio of molar concentrations of ML_m in both phases. The chelate partition constants were determined directly for Sc and Y, and indirectly for Tl as specified below. The distribution ratio D of thallium(III) has been found to decrease with time. After a fast decrease during the first few minutes, reflecting the transfer of Tl(trop)$_3$ from the organic to the aqueous phase, a further continuous, but rather slow drop in D was observed, with the rate practically constant (the half-time being 13−16 min) in the pH range studied (2.0−4.6). This slow decrease was presumably due to the hydration of the uncharged chelate molecule in the aqueous phase, followed by fast hydrolysis of the hydrated thallium(III) species. The hydration is a first-order reaction, followed by further fast transfer of Tl(trop)$_3$ from the organic to the aqueous phase to sustain the transient equilibrium described with the equilibrium constant $P = [\mathrm{Tl(trop)_3}]_{\mathrm{org}}\,[\mathrm{Tl(trop)_3}]_{\mathrm{aq}}^{-1}$. The transfer is thus a first-order reaction as well, and the organic phase concentration of the chelate is (in the interval of the continuous slow drop in D) a function of time (t): $[\mathrm{Tl(trop)_3}]_{\mathrm{org}} = C^0{\cdot}e^{-\lambda t}$, where C^0 is an extrapolated value equal to a hypothetical concentration of the chelate in the organic phase at time zero, assuming the hydration had not started, but the transfer equilibrium had already been established. Provided that the volumes of the organic and aqueous phases are equal to each other, $P = C^0(C_{\mathrm{tot}} - C^0)^{-1}$, where C_{tot} denotes the real initial concentration of the chelate in the organic phase. Extrapolation of the experimental $\log[\mathrm{Tl(trop)_3}]_{\mathrm{org}}$ values to $t = 0$ from the time interval where the dependence was found linear, made it possible for us to evaluate the partition constant for [Tl(trop)$_3$], and the "true" distribution constants when TOPO was present in the system.

Figure 3 shows the logarithms of the relative distribution ratios, $\log(D/D_0)$ or $\log(D/P)$, of metal tropolonates studied, plotted against the total TOPO concentration (C_B). The solid curves are the best-fit functions (weighted least squares), except for the highest C_B values for Tl and Y. The observed increase in D with increasing TOPO concentration means that the chelates, except for [Ga(trop)$_3$],[30] formed adducts with TOPO. However, because of significant tropolone−TOPO association in the organic phase:

$$\mathrm{HL} + \mathrm{B} \xrightarrow{K_{\mathrm{as}}} \mathrm{HL}\cdot\mathrm{B} \qquad (6)$$

where K_{as} denotes the association constant, $[B] < C_B$ and therefore, to calculate adduct stability constants, we must

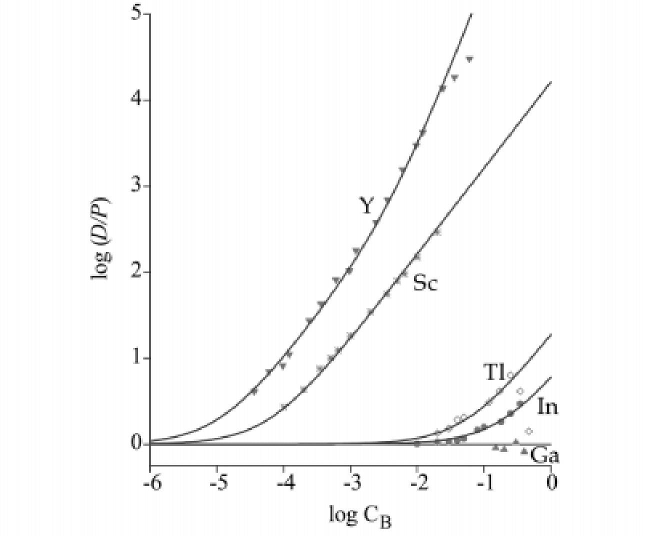

Figure 3. Effect of total molar concentration of TOPO, C_B, on the distribution of tropolonates of gallium, indium, and thallium(III) between carbon tetrachloride and various aqueous phases, and tropolonates of scandium and yttrium between toluene and water at 298.2 K (see Exp. Sect.); in the case of In and Ga, P denotes the distribution ratio, D_0, determined in the absence of either TOPO or tropolone, respectively; the solid lines are the best-fit curves

account for this effect. In contrast, we may neglect a decrease in TOPO concentration due to adduct formation, because of the large excess of TOPO with respect to the metal ions. Thus, the actual $[B]$ values can be calculated[31] as a function of C_{HL}, C_B, K_{as}, and P_{HL}, where C_{HL} denotes the total concentration of tropolone, and P_{HL} − its partition constant (at low experimental pH the dissociation of tropolone in the aqueous phase is negligible). The P_{HL} values were either determined spectrophotometrically (3.9 for the CCl_4/water system), or evaluated (10 for toluene/water). The association constants of the tropolone−TOPO adduct were either determined from the distribution data[32] of tropolone in the solvent−TOPO/water system at pH = 2 ($K_{as} = 2.7 \pm 0.3$ mol^{-1} dm^3 in CCl_4), or estimated based on the former value and on the data of ref.[32] ($K_{as} = 5$ mol^{-1} dm^3 in toluene).

Equation (5) correctly describes the system when the changes in the concentration of B do not affect the $M^{n+} \rightleftarrows ML_n$ equilibrium, i.e. where $D_0 = P$, which is the case for Sc, Y, and Tl. The decrease in the concentration of free tropolone, [HL], in the experiments with $In(trop)_3$ results (at low pH) in some dissociation of the chelate, accompanied by a decrease in the D values. That is because at sufficiently low pH, when the concentration of any charged chelate, $[ML_j]^{m-j}$, in the aqueous phase is negligible in relation to M^{m+}, the extraction equilibrium can be described with the Equation (7) obtained by the transformation of Equation (2).

$$D = K_{ex}[HL]_{org}^{m}[H^+]_{aq}^{-m} \quad (7)$$

The TOPO−tropolone association decreases the original $[HL]_{org,0}$ value to $[HL]_{org}$, therefore the values $D[HL]_{org}^{-m}[H^+]_{aq}^{m}$ and $D_0[HL]_{org,0}^{-m}[H^+]_{aq,0}^{m}$, are to be substituted for D and D_0, respectively, in Equation (5).[31] With this substitution, and assuming that (1) D and D_0 were measured at the same pH, (2) only one TOPO−tropolone associate (1:1) was formed in the organic phase, and (3) a large excess of HL existed with respect to M^{m+}; we could rearrange Equation (5) to Equation (8).

$$\frac{D}{D_0}\left(\frac{C_{HL}}{C_{HL} - C_B + [B]}\right)^m = 1 + \beta_{m,1}[B] + \beta_{m,2}[B]^2 \quad (8)$$

The stability constants (Table 4) were calculated in this way by putting free TOPO concentrations for [B], and by weighted least-squares fitting, Equation (5) for Sc^{3+}, Y^{3+}, and Tl^{3+} ions; and Equation (8) for In^{3+}.

Discussion

Reliability of the Model

The αdik ligand has 23 valence electrons, but their number on the four atoms (O and C) in the 5-membered chelate ring, 21, is the same as that in the tropolonate ligand which has the even number of all valence electrons. The αdik ligand has a high symmetry in the optimised chelate structure, the same as the tropolonate ligand. Although the optimised structures of $[M(\alpha dik)_3]$ and $[M(trop)_3]$ chelates (M = Sc, Y) and the charge distribution on their atoms had appeared similar (Table 1), a question arose, as to whether the αdik ligand, a radical, was a reliable model for tropolonate. Additional calculations were thus carried out for scandium and yttrium chelates with another similar ligand, $O{=}CH{-}CH_2{-}O^-$ (L′), which has an even number of electrons. However, the optimised 5-membered chelate rings formed by L′ appeared asymmetric, with the $M{-}O^{L'}$ distances differing by ca. 20% from each other, and also with two different C−O distances. Two hydrogen atoms at one of the carbon atoms were located out-of-plane of the ligand rings. Also some other differences between $[ML'_3]$ and $[M(trop)_3]$, greater than those between $[M(\alpha dik)_3]$ and $[M(trop)_3]$, allowed us to conclude that the αdik ligand, although a radical, is a good model for tropolonate, and is better than L′.

Another question concerns the possible inadequacy of the computation method used for thallium, the heavy relativistic metal. In fact, the DFT calculations with the use of pseudo-relativistic potentials can hardly be considered as fully relativistic, and their use for heavy metal compounds may result in, e.g. overestimated metal−ligand distances.[33] At the moment, the quality of the computation method used can be verified indirectly (see below). As long as fully relativistic calculations in such extensive systems are extremely troublesome and time consuming, we have to accept the results obtained.

Table 4. Experimental values of partition constants of metal tropolonates, stability constants of their adducts with TOPO, and Gibbs free energies of the 1:1 adducts formation (25 °C, molar concentration scale; energies in kJ mol^{-1}; the uncertainties are equal to two standard deviations)

Chelate	Solvent	P	$\log \beta_{3,1}$ [a]	$\log \beta_{3,2}$ [a]	ΔG_{ad} (1:1)
$Sc(trop)_3$ [b]	toluene	0.381 ± 0.007	4.27 ± 0.03	− [c]	-24.4 ± 0.2
$Y(trop)_3$	toluene	0.0020 ± 0.0003	4.99 ± 0.05	7.39 ± 0.08	-28.5 ± 0.3
$Ga(trop)_3$	CCl_4	38 ± 3	no adduct	−	−
$In(trop)_3$	CCl_4	39 ± 3	0.97 ± 0.10	1.86 ± 0.10	-5.5 ± 0.6
$Tl(trop)_3$	CCl_4	6.8 ± 0.7	1.35 ± 0.08	(0.3 ± 5.9)[c]	-7.7 ± 0.4

[a] Calculated using Equation (5) for Sc, Y, and Tl, and Equation (8) for In. [b] The data from ref.[6], corrected for TOPO−tropolone association. [c] The $\beta_{3,2}$ value could not be determined because of either insufficient TOPO concentration in the experiment (Sc) or the antagonistic effect in solvent extraction at higher TOPO concentrations (Tl).

Structures

The optimised distances and angles in $[Sc(trop)_3]$ correspond very well with the experimental data for the crystalline complex (Table 1). A good agreement was also found between the parameters calculated for $[M(\alpha dik)_3]$ chelates (M = Sc, Ga, In) and the experimental data for crystalline tropolonates[22] and other α-diketonates.[34] Because of no experimental data are available for α-diketonates of thallium(III) (and Y), their aqua complexes can be used for comparison. The $Tl^{III}-O$ distance calculated for $[Tl(\alpha dik)_3]$ is greater (by 4%) than the experimental values in octahedral hexahydrates, both in solution and in the solid (221 to 225.5 pm[35]), while the corresponding differences for Sc,[36] Ga, and In[37] (Y forms octahydrates) are smaller, below 2%.

The analysis of the optimised coordination polyhedra in the adducts (CN = 7)[5] shows that TMPO attacks the chelate molecule (CN = 6; D_3) from the side of its open trigonal face. The coordination of the seventh ligand is accompanied by significant rearrangements in the chelate structure (Table 2). To make room for this ligand, the three αdik ligands have to be contracted, turned, and spread apart (Figure 1b), followed by a decrease in their bite angles and an elongation of the $M-O^L$ bonds. The chelate rings are nonsymmetrically deformed, the three $M-O^L$ bonds adjacent to the $M-O^B$ bond being elongated much more than those opposite the bond were. The extent of distortion of chelate molecules depends on the metal ion radius. The smallest distortion has been found for chelates of large Tl^{3+} and Y^{3+}; the angle between two αdik ligands (medians) adjacent to the $M-O^B$ bond increased by ca 15% in relation to the original one (120°) in the chelates. There are three short (290−320 pm) O^B-O^L distances, one intermediate (330−336 pm), and two long (390−450 pm) in the distorted structures (intermediate between C_{3v} and C_{2v}). For the intermediate-size In^{3+} and Sc^{3+}, the angle between the two αdik ligands increased by ca 22%. There are three or four short (280−310 pm) O^B-O^L distances, one or two intermediate (340−365 pm), and one long (ca 415 pm) in the distorted structures (intermediate between C_{2v} and D_{5h}).

According to the calculations, binding of TMPO by the smallest Ga^{3+} ion in $[Ga(\alpha dik)_3]$ is accompanied by breaking one $Ga-O^L$ bond and opening the chelate ring. Such a picture has not been experimentally confirmed for $[Ga(trop)_3]$, but has been confirmed for another, less stable chelate $[Ga(tta)_3]$ (Htta = 2-thenoyltrifluoroacetone), which forms a TOPO adduct.[31] In no case Ga^{3+} increases its CN to seven. The nonexistence of $[Ga(trop)_3]-TOPO$ adducts may explain the difference in the ability of tris(tropolonates) of gallium and indium to label blood cells[9,10] by an associative reaction within the cell.

Energies

We expected the energy of $[ML_3]$ formation to be affected by two factors: (1) the charge-to-radius ratio of the metal ion, and (2) the availability of vacant d orbitals of the metal ion for hybridisation to a valence state corresponding to CN = 6. The order of decreasing ΔE_{ch} values calculated for the $[M(\alpha dik)_3]$ chelates, Sc > Y > Ga > In > Tl (Table 3), shows that the d^0 ions form much more stable chelates than d^{10} ions, while the expected decrease in chelate stability with increasing ionic radius can be observed only within each group. Thus, the effect of electron configuration prevails over that of radius.

The calculated ΔE_{ad} values give the following order of adduct stability in the gas phase: In < Tl < Sc < Y. This sequence reproduces the experimental order of Gibbs free energies of adduct formation in solution,[38] $\Delta G_{ad} = -RT \ln \beta_{3,1}$. The differences between the ΔE_{ad} and ΔG_{ad} values result from the differences in the reaction media, temperature (0 and 273.2 K), and above all from the entropy term that contributes to ΔG_{ad} only, and can be large.[39] With all these differences, the correlation between ΔE_{ad} for $[M(\alpha dik)_3]$ and ΔG_{ad} for $[M(trop)_3]$ (Tables 3 and 4) is quite reasonable. Moreover, the differences between the values for the two tropolonates (of yttrium and scandium), $\Delta(\Delta E_{ad}) = -5.5$ kJ mol^{-1} and $\Delta(\Delta G_{ad}) = -4.2$ kJ mol^{-1}, are fairly similar.

The experimental data on the 1:1 and 1:2 TOPO adducts of metal tropolonates (CN = 7 and 8) correspond well with the data on anionic $[M(trop)_4]^-$ complexes;[6,40] more stable for Y and Sc, and less stable for In.[40] Much greater stability of the adducts of the d-block than p-block metal ions betokens the primary importance of electron configuration of the metal center. Only further, in each group, is the adduct stability differentiated according to the radii of metal ions. Moreover, the sequences of ΔE_{ad} values are reversed when compared with those of ΔE_{ch}, i.e. the effect of ionic radius on the stability of the adducts (CN = 7) is opposite to that observed for the chelates (CN = 6).[41] This can be explained in terms of differences in distortion energies of the chelates formed by small and large ions of the same charges upon coordination of the seventh ligand. These differences are due to stronger $M-O^L$ bonds and the lesser flexibility of ligands in the chelates of small ions.[6] Greater distortion energies observed for the chelates of small ions (Sc, In) compared to those of large ions (Y, Tl) (Table 3) overcompensate the stronger attraction of the ligand by the small cations.

Character of the M−O Bonds; Hypervalence

Less stable $[ML_3]$ chelates and $[ML_3\cdot TMPO]$ adducts of the d^{10} ions do not necessarily imply that the high-lying (cf. the calculated promotion energies) virtual *n*d orbitals of the $(n-1)d^{10}$ ions participate in bonding. General considerations suggest that the use of these distant *n*d orbitals in bonding is unlikely.[42] Molecular orbitals of such a complex with e.g. six ligands can be formed using only four orbitals of the central ion (s and p) and six ligand orbitals. Thus, four bonding and four antibonding MOs are formed, and the two ligand orbitals remain nonbonding. This results in a lowering of the average bond order and a decrease in the electron population in the $M-O^L$ bond region, therefore in less stable hypervalent (or hypercoordinate) complexes.[42] The binding of the seventh ligand to the hypervalent chelate should additionally decrease the electron population of the $M-O^L$ bonds in the adduct by $^1/_7$. This has been observed for In and Tl, where the $M-O^L$ populations in the TMPO adducts are about 14% less than those in the corresponding chelates (Tables 1 and 2), in contrast to the Sc and Y adducts, where the $M-O^L$ populations remain practically the same as those in the chelates. Therefore, we suppose that the adducts formed by In and Tl chelates are also hypercoordinate, with their bonding MOs formed only from the *n*s and *n*p orbitals of the d^{10} ions, with no participation of either filled $(n-1)$d or virtual *n*d orbitals. In contrast, Sc and Y chelates form stronger "normal" adducts with seven bonding MOs in which the vacant $(n-1)$d orbitals of the metal do participate. Indeed, the analysis of charge distribution on the metal ions (q_M in Tables 1 and 2) shows that the d-block ions accept some electron density from TMPO in the adducts, in contrast to the p-block metals that increase their positive charge in the adducts. Also, the analysis of the electron population of basis metal AOs contributing to bonding ($M-O^L$) MOs in the chelates betokens a contribution from the d orbitals of scandium and yttrium, but none from those of indium and thallium. The same has been observed in the case of the adducts ($M-O^B$ bonding). The expansion coefficients of the bonding MOs show that the d orbitals of Sc and Y in the adducts accept practically the whole charge equal to the difference (ca. 0.03 a.u.) between the Δq values calculated for the adducts of d-block and p-block metals (Table 2).

Rather high electron population in the $In-O^L$ bonds (the population on the $Tl-O^L$ bonds is low, as expected) can be explained in terms of incomplete screening from nuclear charge by the filled d^{10} shell, which increases the effective charge on the p-block ion, and also the population of the bonds. This is in line with the high negative $\Delta E_{d,ch}$ and ΔE_{int} values for In (Table 3). The lack of unoccupied $(n-1)$d indium orbitals able to accept the electron density makes the $M-O^L$ charge separation in $[In(\alpha dik)_3]$ the highest (Table 1), i.e. the smallest shift of electron density from the ligands to the metal ion. On the other hand, particularly strong stabilisation of thallium 6s and $6p_{1/2}$ orbitals, due to the presence of filled 4f shell and relativistic effects,[43] should result in a greater shift of electron density from the ligands to these orbitals, which is the reason for the low positive charge on the Tl^{III} ion in the chelate, and for the small electron population of the $Tl-O^L$ bonds.

In all the adducts, the $M-O^B$ bond is significantly shorter than the $M-O^L$ bonds, though this is not reflected in the bond populations (Table 2). A possible reason for shortening the $M-O^B$ bond is its partially π-bond character, as discussed below. Its lower electron population can be due in turn to the lack of charge on the TMPO ligand, whereas the αdik ligands are negatively charged. In any case, the In and Tl adducts studied give us an interesting case of hypervalent bonding strengthened by π-bonding.

Molecular Orbitals

The examination of the system, by means of MOLDEN, shows that there exist sets of lower lying multi-centred bonding MOs of σ symmetry, responsible for the formation of TMPO adducts of yttrium and scandium chelates. In the yttrium adduct, these strongly bonding MOs (ca. −1.0 a.u.) are formed from the MOs of the chelate (−0.957 a.u.) and TMPO (−0.923 a.u.), with the contribution from AOs of the metal (s and p, ca. 25%) and oxygen atoms only. In the scandium adduct, these MOs (ca. −1.3 a.u.) are weakly bonding because they are formed almost entirely from the metal orbitals. The indium and thallium adducts have no bonding MOs in the region of lower energies. The only orbitals in the latter (ca. −0.75 a.u.) are practically pure, occupied AOs (d) of thallium, while there is no contribution from indium AOs in the former.

In all the adducts there are higher lying (ca. −0.41 a.u.) bonding MOs of σ symmetry (Figure 2a). They are more strongly delocalised (apart from mainly the O atoms, they also extend to the C atoms), and are formed with the participation of occupied orbitals of σ symmetry, the HOMO (ca. −0.22 a.u.) of the chelates and the HOMO−2 (−0.3317 a.u.) of TMPO. Unexpectedly, the latter does not describe a lone electron pair on the O^B atom, but the σ-electron pair of the O=P bond. The energy gain is due to redistribution of the electron densities of both MOs over the delocalised orbitals. This rather unusual picture can be explained assuming that (1) the lone electron pairs on the O^B atom participate in another bonding, and (2) the O^B

atom changes its valence state and hybridisation from sp^2 in the free TMPO molecule to sp^3 or rather sp^m in the adduct (m is a fractional value smaller than 3). The former assumption is in line with the short O^B-O^L distances. The latter explains why the shift of electron density from the P=O to the $M-O^B$ bond region is large (Table 2). The most important, however, is the observation that the contribution from the metal AOs to these multi-centred bonding MOs in the adducts is quite different for the d- and p-block metals. This contribution is equal to about 7% from the d orbitals of Sc and Y, but none from those of In and Tl, in line with the hypothesis of hypervalent character of their adducts.

The expected additional bonding between TMPO and the chelates has been exemplified by another set of bonding MOs found in each adduct, higher lying (ca. −0.29 a.u.), of symmetry typical for π-type interactions (Figure 2b). These MOs are greatly delocalised; their electron density extends over the whole adduct molecule, in particular the O^B and O^L atoms. These MOs are formed from orbitals of the same symmetry, presumably with the chelate LUMO localised mainly on the O^L atoms (ca. −0.13 a.u.), and the TMPO doubly degenerate HOMO (−0.2336 a.u.) that accommodates two lone electron pairs localised on the TMPO oxygen atom. This π-type interaction between the two lone electron pairs and the αdik ligands enhances the deformation of the adduct molecule and increases the MOP angle to 130−140°, as calculated.

The energies of both σ- and π-type bonding MOs in the adducts (Table 3) are closer to the energies of the original MOs in TMPO, not in the chelates. This is in line with the earlier conclusion (based on Δq values) that the TMPO electrons are mainly responsible for the TMPO − chelate bonding. The moderate asymmetry of this bond together with the results of bond population analysis (Table 2) shows that both the extent of covalence and of the ionic character determine the bond character.

Conclusions

Both density-functional calculations and experimental data show that the coordination number of the central metal ion in the studied neutral chelates with bidentate ligands increases from six to seven (or even eight) upon formation of inner-sphere molecular adducts with a monodentate strong electron-donor ligand. Noteworthy is a good correspondence between the computational and experimental data both in structural parameters of the chelates and in the energies of adduct formation. The method used permits not only the calculation of reasonable values of the energies, but also their separation into contributions related to mutual interactions of electron clouds of both components, and to the structural distortion of the components that accompany adduct formation.

The tendency to increase the CN from 6 to 7 depends strongly on the metal ion, in particular on its radius and electron configuration − the larger the radius, i.e. the larger the space accessible to the seventh donor atom, the smaller the energy required for distortion of the chelate structure, and in consequence the greater the tendency to form adducts. The energy of chelate distortion strongly differentiates the metal ions with respect to adduct stability. If the ion is too small, the chelate does not form adducts at all, as exemplified by gallium tropolonate.

On the other hand, much greater tendency to increase the CN by metal ions of d-block than those of p-block points out the problem of high energy gaps between the *n*s, *n*p, and *n*d orbitals, which is not the case with empty ($n-1$)d orbitals in the d^0 ions. High promotion energy makes it rather unlikely that the distant virtual *n*d orbitals could be used for hybridisation, corresponding to CN = 5 and more. Instead, the assumption on the formation by p-block metal ions of hypervalent compounds, with no participation in bonding of metal d orbitals, satisfactorily explains why the chelates (CN = 6) of d^{10} metal ions and their TOPO adducts (CN = 7 or 8) are less stable than the related compounds of d^0 ions.

The analysis of the molecular orbitals calculated for the adducts and for their components allows the identification of the orbitals contributing to adduct formation, and the description of the bond between the components as having both σ- and π-type character. The σ-type bond is formed with no participation of the lone electron pair on the donor oxygen atom in the TOPO molecule but of another pair already engaged in double bonding, therefore, in order to form the bond, the oxygen atom must change its original hybridisation. The π-type bonds are formed by transferring electron density from the lone electron pairs of the TOPO oxygen atom to the vacant orbitals on the donor oxygen atoms of the bidentate ligands. This additional π-bonding strengthens the bond and stabilises the adduct.

Some unexpected characteristics calculated for the compounds of d^{10} ions, especially of indium, are probably due to the occupancy of the metal ($n-1$)d orbitals, which hinder the transfer of electron density to the metal ions, in contrast to the compounds of d^0 ions. Quite effective transfer of electron density to the thallium(III) ion can be explained in terms of the relativistic properties of this heavy metal.

Experimental Section

General Remarks: Distribution ratios were calculated from direct measurements of specific radioactivity of both phases using an NaI(Tl) well-type detector (^{72}Ga and ^{114m}In), and a Geiger−Müller counter (^{90}Y, ^{204}Tl). The radiotracers were supplied by the Centre for Isotope Production at Swierk, Poland. Tropolone, 1-hydroxycyclohepta-3,5,7-trien-2-one, Htrop (98%, Aldrich), was used as received. TOPO (p.a., Merck) was purified[6] by repeated (up to six times) washing its concentrated stock solutions in heptane or toluene with 5% aqueous sodium carbonate solution and water. Carbon tetrachloride (p.a., POCh Gliwice) was washed and distilled. Toluene (p.a., POCh Gliwice) was used as received. Doubly distilled water was used throughout. Distribution of tropolone between water (pH = 2) and carbon tetrachloride (+ TOPO) was studied by shaking the solutions followed by absorbance measurements of dilute aqueous solutions of tropolone (original and at equilibrium) in quartz cells at 345 nm at pH = 1. − pH: Orion 720A with a glass-calomel combination electrode calibrated against standard reference buffers. UV/Vis: Beckman DU-68.

Solvent Extraction Procedure: The organic phase was prepared immediately before extraction. After the radiotracer was added to the equilibrated aqueous phase, the pH was adjusted with either H_2SO_4 (Tl: pH = 2.6) or HCl (Ga: 2 mol dm^{-3}; In: pH = 1.5; Y: pH = 4.5) and the system was re-equilibrated. Thallium(I) was previously oxidised in 2 mol dm^{-3} H_2SO_4 with $Na_2S_2O_8$ (10^{-3} mol dm^{-3} Ag^+).[44] The concentration of indium and thallium carriers was kept in the range 10^{-5}−10^{-4} mol dm^{-3}, that of scandium and gallium in the range 10^{-6}−10^{-5} mol dm^{-3}, and ^{90}Y was carrier-free. The initial concentration of tropolone in carbon tetrachloride was either 0.1 mol dm^{-3} (Tl) or 0.01 mol dm^{-3} (Ga and In), and in toluene either 0.01 mol dm^{-3} (Y) or 0.02 mol dm^{-3} (Sc). The phases were shaken for 30 min until the distribution equilibrium was attained, separated, and then the specific activities of aliquots were measured. The loaded (Sc, In) organic phase was contacted again with a freshly pre-equilibrated aqueous phase containing no metal and the procedure was repeated. The *D* values (see Supporting Information) determined in both extraction and back-extraction steps differed from each other by less than 5%.

The partition constant and "true" distribution ratios for Tl(trop)$_3$ were determined in back-extraction experiments with the thallium-loaded organic phase and fresh, no thallium-containing, aqueous phase of pH ≈ 2.6. The phases were continually shaken and the aliquot samples were collected at ca. 5−10 min intervals in the range from 10 to 45 min (see Supporting Information). Partition constants of the other tropolonates have been determined independently in the plateau regions,[6] i.e. $4 < \mathrm{pH} < 6$. The data for scandium are taken from our recent paper.[6] The extraction experiments were carried out at 298.2 ± 0.2 K.

Acknowledgments

We thank Professor J. Konarski (Poznan) and Dr. J. Burgess (Leicester) for their critical reading of the manuscript and for valuable comments. The research was supported in part originally by the Polish Committee for Scientific Research (KBN) under grant nr. 3 T09A 016 09 and then by the Institute of Nuclear Chemistry and Technology. The numerical calculations were carried out at the Interdisciplinary Centre for Mathematical and Computational Modelling, Warsaw, and the Poznan Supercomputing & Networking Centre. We acknowledge obtaining access to the computer resources and the kind cooperation of the staff.

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[27] The total energies of the adduct components (subunits − chelate and TMPO) were calculated after moving away the subunits (the distance of 600 pm was thought sufficient to neglect the effects of all interactions between the two components − electrostatic, charge transfer etc.) In this new system the $M-O^B$ bond was broken, but the geometry of the subunits was maintained the same as that in the adduct. The total charges (Δq) on all the atoms of the separated subunits were equal to zero, contrary to the case when in the adduct.

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a set of corrected D values for gallium, each very close to D_0 (equal to 0.905) over the whole range of TOPO concentrations studied (Figure 2). This shows that [Ga(trop)$_3$] formed no TOPO adducts.

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Received November 21, 2000
[I00441]