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Complexes of In(III) with Tetraphenylimidodiphosphinate Ligands**

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Abstract. We report the synthesis and characterization of the inorganic heterocyclic complexes In(OP*Ph*$_2$NP*Ph*$_2$O)$_3$ and In(SP*Ph*$_2$NP*Ph*$_2$S)$_3$. The structure of the sulfur derivative was determined by X-ray methods. The complex presents a distorted Oh symmetry and it is compared with the Bi(III) analog. The ^{31}P-NMR data and the X-ray structural determination suggest that the bulky ligands are responsible for the geometrical features in these complexes and therefore, for the Bi(III) analogs perhaps the lone pair does not play an important role in the structure.

Keywords. Indium complexes; Tetraphenylimidodiphosphinates; Inorganic rings; Wynne's theory.

Komplexe von In(III) mit Tetraphenylimidophosphinat-Liganden

Zusammenfassung. Es wird über die Synthese und Charakterisierung der anorganischen heterocyclischen Komplexe In(OP*Ph*$_2$NP*Ph*$_2$O)$_3$ und In(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ berichtet. Die Struktur des Schwefelderivates wurde mit röntgenographischen Methoden bestimmt. Der Komplex gehört einer verdrillten Oh Symmetrie an und wird mit dem Bi(II)-Analog verglichen. Die ^{31}P-NMR-Daten und die Röntgenstruktur legen nahe, daß die raumbeanspruchenden Liganden für die Geometrie dieser Komplexe verantwortlich sind und daher bei der Struktur des Bi(II)-Analogen die freien Elektronenpaare eine untergeordnete Rolle spielen.

Introduction

Inorganic (carbon free) chelates are members of the larger family of inorganic hetero-(metallo)-cycles. This area of inorganic chemistry is beginning to be recognized as a self-consistent part of coordination chemistry [1]. The tetraphenylim-

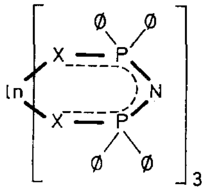

Fig. 1. Indium(III)-tetraphenylimidodiphosphinates; *X*=O,S

** Dedicated to Prof. Dr. Heinrich Nöth

idodiphosphinates (Fig. 1), in its oxygen and sulfur derivatives, are powerful β-difunctional ligands, sterically unencumbered about the donor atom, are ideal to study the variations in stereochemistry of the metal complexes through the formation of inorganic metallocycles. The interest in such ligands is generated by the unusual coordination modes and the stereochemistry of the chelate rings. The presence of $M\mathrm{S}_n$ cores has important bioinorganic implications [2], and the oxygenated derivatives produce "inorganic β-diketonates" [3]. In spite of the interest in the inorganic rings and cages [4], the literature of the complexes of the main group metals with these ligands is very scarce and is limited to groups 14 (Sn and Pb), 15 (Bi), 16 (Se, Te) and the $\mathrm{Be(O}Ph_2\mathrm{PN}Ph_2\mathrm{O})_2$ complex [1].

The Bi(III) complexes with the title ligands have been obtained by Williams [5, 6] in order to test Wynne's theory about the stereo chemistry of the non-bonded lone pair in $\mathrm{AX_6E}$ systems [7]. In this aspect both the $\mathrm{Bi(OP}Ph_2\mathrm{NP}Ph_2\mathrm{O})_3$ and $\mathrm{Bi(SP}Ph_2\mathrm{NP}Ph_2\mathrm{S})_3$ show only a single ^{31}P-NMR signal, but the oxygen complex presents a peak much broader than that observed for the sulfur analog, this situation is indicative of some non-octahedral site in solution for the oxygen complex and an almost octahedral symmetry in solution for the sulfur compound in agreement with Wynne's theory. The X-ray structure determination of the sulfur derivative presents an "enigmatic distortion pattern", perhaps resulting from two opposing effects, the electrostatic repulsions between bonded pairs and the lone pair and the presence of bulky lignads forcing a near octahedral symmetry [6].

In this paper we report the synthesis and characterization through elemental analyses, IR, ^{31}P-NMR, of the In(III) complexes, $\mathrm{In(OP}Ph_2\mathrm{NP}Ph_2\mathrm{S})_3$ and $\mathrm{In(SP}Ph_2\mathrm{NP}Ph_2\mathrm{S})_3$ (Fig. 1) as well as the X-ray structure determination of the second complex, in order to obtain the coordination mode of the imidodiphosphinate entity and to compare the complexes with the Bi(III) analogs in a situation without lone pairs. These complexes correspond to the first examples of group 13 complexes with tetraphenylimidodiphosphinate ligands.

The $\mathrm{InS_6}$ cores are well established with diverse ligands and the structures correspond to the distorted Oh [8] or trigonal prismatic [9] symmetry group.

Experimental Part

Chlorodiphenylphosphine and 1,1,1,3,3,3-hexamethyldisilazane were obtained from Aldrich C. C., $\mathrm{InCl_3}$ from Ventron. The solvents were distilled and dried before use. $[Ph_2\mathrm{PONP(OH)}Ph_2]$ and $[Ph_2\mathrm{PSNHPS}Ph_2]$ were prepared according to the literature [10]. The corresponding potassium salts were obtained by the method of Schmidpeter [11].

Infrared spectra were recorded on a Perkin-Elmer 283-B spectrometer as KBr pellets and Nujol mulls, phosphorus-31 NMR were obtained on a Jeol FX 90 instrument. 85% phosphoric acid was used as an external reference. C, H and N analyses were obtained in commercial labs. Phosphorus was determined by the gravimetric method as ammonium molybdophosphate and the indium content as $\mathrm{In_2O_3}$.

Synthesis of the Complexes

Tris-[N-(diphenylphosphinyl)-P,P-diphenylphosphinic amidato-0,0′]-indium(III). To a solution of $\mathrm{InCl_3}$ (1 mmol) in *Me*Oh was added a solution of $\mathrm{K(OP}Ph_2\mathrm{NP}Ph_2\mathrm{O})$ (3.5 mmol) also in methanol. The mixture of reaction was refluxed for 30 min. After that the solid obtained was filtered, washed with methanol, $Et_2\mathrm{O}$ and dried in air. Yield (55%). Calcd. for $\mathrm{C_{72}H_{60}InN_3O_6P_6}$: C 63.5, H 4.4, N 3.18, P 13.6, In 8.4. Found C 62.9, H 4.5, N 3.1, P 13.2, In 8.5. $\delta(^{31}\mathrm{P})$ −25.37 ppm. IR, $\nu\mathrm{P_2N}$ 1 222 cm^{-1}.

Tris-[N-(diphenylphosphinothioyl)-P,P-diphenylphosphinothioic-amidato-S,S′]-indium(III). The synthesis of this complex was similar to that dexcribed for the O,O′ analog. Yield (75 %). Calcd. for $C_{72}H_{60}InN_3P_6S_6$: C 59.2, H 4.1, N 2.9, P 12.7, In 7.9. Found C 60.1, H 4.2, N 2.9, P 12.3, In 7.9 $\delta(^{31}P)$ -34.93 ppm. IR, νP_2N 1 245 cm^{-1}.

Crystals suitable for X-ray analysis of the $In(SPPh_2NPPh_2S)_3$ complex were obtained in the following way: The compound was dissolved in CH_2Cl_2, and ethanol was added. Upon the slow evaporation of the mixture white crystals were obtained. In spite of the use of different methods of growing crystals we were unable to obtain high quality crystals, and this is reflected in the limited accuracy of the refinement; however, the questions concerning the coordination chemistry of the complex as well as the geometrical features can be fully answered.

X-ray-Analysis of $In(SPPh_2NPPh_2S)_3$

A colorless plate-like crystal of $C_{72}H_{60}InN_3P_{60}S_{60}$ having c.a. dimensions 0.06 × 0.24 × 0.38mm was mounted on a glass fiber. All measurements were made on a Nicolet R3m diffractometer with graphite monochromated Mo Kα radiation. Cell constants obtained from least-squares refinement using the setting angles of 19 carefully centered reflections in the range $3.88 < 2\Theta < 15.89°$ correspond to an monoclinic cell with dimensions a = 16.053(4), b = 20.554(14), c = 21.089(12) Å, β = 97.91 (4)°, $V = 6892(11)$. Space group uniquely determined from systematic absences P_{2_1}/a for z = 4 and FW 1460.31. The calculated density is 1.407.

The data were collected using the $w-2\Theta$ scan mode to a maximum 2Θ value of 50°. Of the 13 076 reflections collected, 12 240 were unique. The data were corrected for Lorentz and polarization effects. A decay correction based on the measurements of two standard reflections showing an average variation of -7.9% was also applied. No absorption correction [$\mu(MoK\alpha) = 6.7\,cm^{-1}$] was applied.

The structure was solved by a heavy-atom method. The non-carbon atoms excluding the hydrogen atoms were also refined anisotropically (carbon atoms were refined isotropically and hydrogen atoms were included in idealized positions with a temerature factor 1.2 times the B_{eq} value of the atom to which they were bonded). The final cycle of full-matrix least-squares refinement was based on 3 242 observed reflections [$I > 3.00\sigma(I)$] and 441 variable parameters with unweighted and weighted agreement factors of $R = 0.1467$, $R_w = 0.1450$. Neutral atom scattering factors were taken from Cromer and Weber [12], anomalous dispersion effects included. All calculations were performed by using the TEXSAN crystallographic software package [13].

Results and Discussion

The compounds obtained were white solids, air-stable, soluble in solvents such as CH_2Cl_2, acetone, etc. but insoluble in H_2O, *Me*OH, *Et*OH, hexane, etc. According to the analytical data they correspond to non-solvated complexes, $In(XPPh_2NPPh_2X)_3$, (X = O,S). The ^{31}P-NMR spectra of both complexes exhibit only one peak, as expected for high symmetrical compounds. The peak of the sulfur derivative is much broader ($w_{1/2} = 0.468$ ppm) than that observed in the oxygen derivative ($w_{1/2} = 0.156$ ppm). In the case of the Bi(III) analogs [5], the narrow peak corresponds to the S,S′ derivative ($w_{1/2} \leqq 0.2$ ppm), the wide one to the O,O′ derivate ($w_{1/2} = 0.6$ ppm) which is opposite to the In(III) compounds reported here. The singlet in the ^{31}P-NMR for $In(XPPh_2NPPh_2X)_3$ (X = O,S) reflects for both complexes a high symmetrical equilibrium in solution. Moreover, the broadness of the resonance signals may indicate a rapid exchange of non-equivalent positions for the sulfur complex. Briefly we can say that the relation between the broadness of the bands for the ^{31}P-NMR spectra and Wynne's theory as postulated by Williams for the Bi(III) compounds [5] as due to the lone pair presence in the Bi(III) ion do not coincide with the NMR results for the In(III) complexes which do not possess a lone electron pair.

Table 1. Positional parameters and *B*(*eq*) of non-C and non-H atoms in $\mathrm{In(SP}Ph_2\mathrm{N}Ph_2\mathrm{PS)_3}$

Atom	*x*	*y*	*z*	*B*(*eq*)
In	0.2485(1)	0.5496(2)	0.7218(1)	4.8(1)
S_1	0.2532(8)	0.4818(8)	0.8249(6)	12(1)
S_2	0.0808(5)	0.5585(8)	0.7127(5)	8.4(7)
S_3	0.2325(6)	0.4536(6)	0.6387(5)	6.0(6)
S_4	0.2267(6)	0.6350(6)	0.6296(4)	5.7(6)
S_5	0.4126(5)	0.5465(6)	0.7296(5)	5.1(5)
S_6	0.2469(6)	0.6566(6)	0.7941(5)	7.4(7)
P_1	0.1713(7)	0.4074(7)	0.8115(5)	7.3(7)
P_2	0.0390(7)	0.4624(9)	0.7161(5)	8.6(8)
P_3	0.3143(5)	0.4722(4)	0.5780(5)	2.8(5)
P_4	0.3128(5)	0.6177(5)	0.5711(4)	3.6(5)
P_5	0.4562(5)	0.5509(7)	0.8250(5)	5.2(6)
P_6	0.3456(6)	0.6492(7)	0.8646(5)	6.2(7)
N_1	0.097(2)	0.412(2)	0.757(1)	8(2)
N_2	0.336(1)	0.540(2)	0.561(1)	5(2)
N_3	0.400(2)	0.582(2)	0.868(2)	8(2)

Table 2. Selected bond legths (Å) and angles (deg) with standard deviations in parentheses for $\mathrm{In(SP}Ph_2\mathrm{N}Ph_2\mathrm{PS)_3}$

In-S_1	2.57(1)	In-S_4	2.61(1)
In-S_2	2.68(1)	In-S_5	2.617(8)
In-S_3	2.63(1)	In-S_6	2.68(1)
S_1-P_1	2.01(2)	S_4-P_4	2.01(1)
S_2-P_2	2.09(2)	S_5-P_5	2.04(1)
S_3-P_3	1.99(1)	S_6-P_6	2.02(1)
P_1-N_1	1.55(3)	P_4-N_2	1.67(3)
P_2-N_1	1.56(3)	P_5-N_3	1.50(4)
P_3-N_2	1.48(3)	P_6-N_3	1.63(4)
S_1-In-S_4	168.4(5)	S_1...S_4	5.157
S_2-In-S_5	177.5(4)	S_2...S_5	5.295
S_3-In-S_6	171.3(3)	S_3...S_6	5.293
S_1-In-S_2	90.6(4)	S_1...S_2	3.734
S_1-In-S_3	98.4(5)	S_1...S_3	3.930
S_1-In-S_5	91.2(4)	S_1...S_5	3.710
S_1-In-S_6	88.0(5)	S_1...S_6	3.651
S_2-In-S_3	89.9(4)	S_2...S_3	3.751
S_2-In-S_4	82.6(4)	S_2...S_4	3.488
S_2-In-S_6	84.1(4)	S_2...S_6	3.587
S_3-In-S_4	91.0(3)	S_3...S_4	3.735
S_3-In-S_5	91.6(3)	S_3...S_5	3.763
S_4-In-S_5	95.4(3)	S_4...S_5	3.865
S_4-In-S_6	82.0(3)	S_4...S_6	3.469
S_5-In-S_6	94.2(3)	S_5...S_6	3.879

Tables 1 and 2 show the positional parameters and selected bond distances and angles for the complex $In(SPPh_2NPPh_2)_3$. Fig. 2 shows the coordination sphere without the phenyl rings. The molecule is discrete and the coordination geometry is better described as a distorted octahedron quite similar to the $Bi(SPPh_2NPh_2PS)_3$ analog [6], although both complexes are not of C_3v symmetry, observed for $Bi[S_2P(OC_3H_7)_2]_3$ [14]. The complex here described possesses two sets of metal-sulfur distances, one of them formed by four In-S bonds with a bond average of 2.607 Å. The other set is formed by two In-S Bonds with a bond average of 2.68 Å. This situation is somewhat different with $Bi(SPPh_2NPPh_2S)_3$

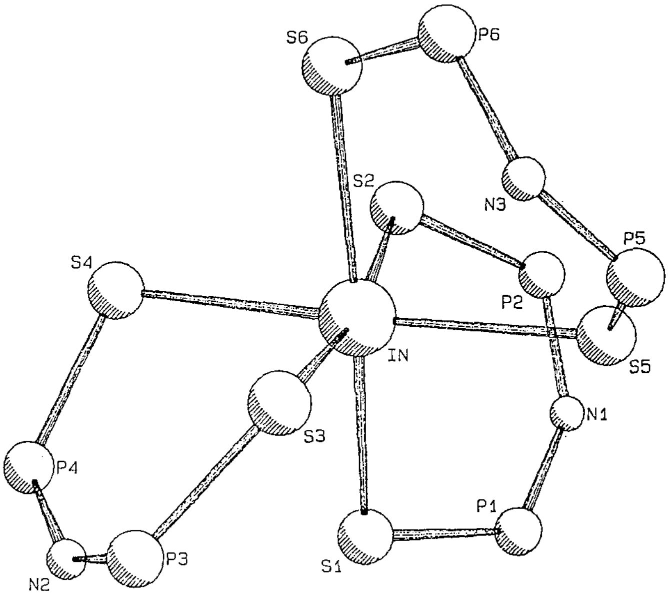

Fig. 2. Prespective view of $In(SPPh_2NPPh_2S)_3$ (phenyls have been omitted for sake of clarity)

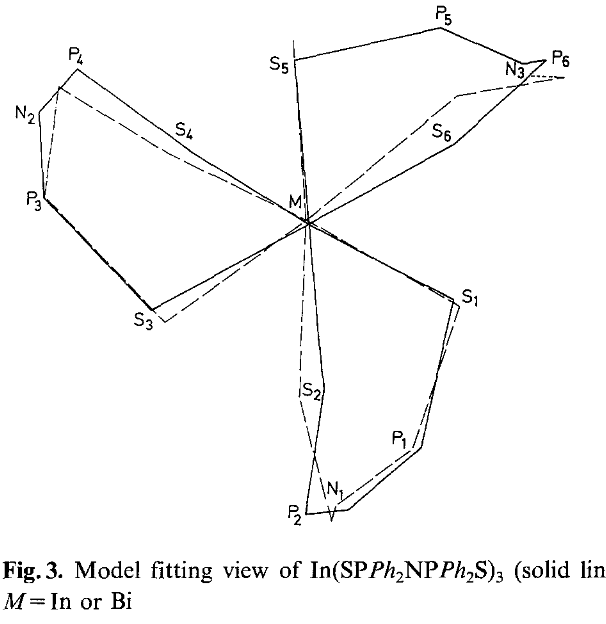

Fig. 3. Model fitting view of $In(SPPh_2NPPh_2S)_3$ (solid line) and $Bi(SPPh_2NPPh_2S)_3$ (dashed line); M = In or Bi

which also possesses two distinct sets of Bi-S bond distance, with one set of three Bi-S bonds longer than the other three Bi-S bonds, a situation somewhat different to the In(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ environment described above. However, the general structure of Bi(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ and In(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ is almost identical, as shown in the model fitting of Fig. 3 with a root mean square deviation (rms) of 0.293. In both complexes the chelate ring is a twisted boat. The average distance for In-S is 2.63 Å, which is not significantly different from other reported values (2.607 Å in In[S$_2$P(O*Et*)$_2$]$_3$ [8]). The S---S distance corresponds to an average value of 3.783 Å, a little shorter than the value in Bi(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ (3.98 Å), but in the range 3.67 to 4.03 Å present in the structures of other complexes of this ligand [15]. Moreover, the average of the S-P and P-N lengths, 2.026 Å and 1.565 Å, respectively, falls in the expected range [1] and is indicative of the double bond character [15].

From the comparison of the ^{31}P-NMR results and the almost identical structure of In(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ and Bi(SP*Ph*$_2$NP*Ph*$_2$)$_3$ complexes we can say that the arrangement in these main group tetraphenylimidodiphosphinates is the result of the presence of bulky ligands forcing an almost octahedral symmetry. Furthermore, we can say that the lone pair does not play an important role in the geometry of the Bi(SP*Ph*$_2$NP*Ph*$_2$S)$_3$ complex.

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