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Reaction of R_3AsI_2 (R = Me or Et) with zinc metal powder to produce $ZnI_2(AsMe_3)_2$ and $[ZnI_2(AsEt_3)]_2$, the first tertiary arsine complexes of zinc(II)

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The reaction of Et_3AsI_2 with zinc metal powder produced the dimeric complex $[ZnI_2(AsEt_3)]_2$, whereas that of Me_3AsI_2 gave equimolar quantities of $ZnI_2(AsMe_3)_2$ and ZnI_2, the latter being identified by X-ray powder diffraction. Both arsine complexes have been structurally characterised and as such represent the only examples for zinc(II). A structural change is thus seen on changing the R groups on the R_3AsI_2 compound. The complex $ZnI_2(AsMe_3)_2$ represents the sole example of a bis(ligand) complex of zinc(II) containing a Group 15 donor atom. Both complexes contain the zinc atoms in essentially tetrahedral geometry but significant distortion is noted for $ZnI_2(AsMe_3)_2$, which may be the result of unfavourable steric interactions.

In contrast to cadmium and mercury,[1,2] the co-ordination chemistry of zinc(II) with Group 15 donors has received little attention, despite the fact that such complexes containing tertiary phosphine ligands were first reported nearly fifty years ago.[3,4] In the case of the co-ordination compounds formed between zinc(II) halides and tertiary phosphines two structural modifications were postulated, the bis(phosphine) complexes, ZnX_2L_2, and the mono(ligand) complexes $(ZnX_2L)_2$. It was believed that steric factors may be fundamental in determining which structure is formed; in the case of tertiary phosphines of low steric requirements a bis(phosphine) complex would be favoured, whereas tertiary phosphines of high steric requirements would favour the mono(ligand) complex, thus relieving steric crowding at the zinc(II) centre. Such a theory seems reasonable and is in agreement with Tolman's cone-angle theory.[5]

However, attempts by Goel *et al.*[6] to prepare the bis(phosphine) complex $ZnX_2\{P(C_6H_{11})_3\}_2$, first claimed by Moers and Langhout,[7] resulted in the isolation of the mixed phosphine–phosphite oxide complex $ZnX_2\{P(C_6H_{11})_3\}\{OP(C_6H_{11})_3\}$, thus casting doubt on the existence of the bis(phosphine) complexes. The only other evidence for the formation of bis(phosphine) complexes is a spectroscopic study of the compounds $ZnX_2(PR_3)_2$ (R_3 = Et_3 or Et_2Ph; X = Cl, Br or I) by Ferguson and Helveldt.[8]

The mono(ligand) complex $[ZnI_2(PEt_3)]_2$ was finally structurally characterised by single-crystal X-ray diffraction in 1992 by our group[9] after having been synthesized from the novel reaction of Et_3PI_2 with zinc metal powder in diethyl ether solution [equation (1), r.t. = room temperature]. The fact that

$$Et_3PI_2 + Zn \xrightarrow[Et_2O,\ N_2]{r.t.,\ 1\ h} [ZnI_2(PEt_3)]_2 \qquad (1)$$

this complex contains a tertiary phosphine ligand of low steric requirements and a mono(ligand) structure is revealed casts further doubt on the existence of the bis(phosphine) complexes, $ZnX_2(PR_3)_2$, and could suggest that previous reports of such complexes are erroneous, and in fact concern the mixed-ligand species $ZnX_2(PR_3)(OPR_3)$ as originally proposed by Goel *et al.*[6]

The co-ordination chemistry of zinc(II) with ligands containing heavier Group 15 donor atoms is non-existent and we therefore decided to employ our synthetic method of treating the compounds R_3AsI_2 (R = Me or Et) with zinc metal powder to produce examples of zinc complexes containing tertiary arsine donor ligands. The reasons for doing this were as follows: first, no such compounds are currently known; secondly, we were intrigued to know if we could synthesize an example of the elusive bis(ligand) complex $ZnX_2(AsR_3)_2$ and structurally characterise this material; finally, we have already illustrated that novel metal complexes are available from our new synthetic route. For example, we have produced novel isomers of known compounds, *e.g.* $[MnI_2(PPhMe_2)]$;[10] compounds with the metal in an unusually high oxidation state, *e.g.* $[NiI_3(AsMe_3)_2]$,[11] some cationic species,[12] *e.g.* the linear $[Ph_3As–I–I–I–AsPh_3]^+$[13] and metal complexes unavailable by conventional synthetic techniques, *e.g.* $[CoI_3(SbPh_3)_2]$.[14] Therefore, the possibility of synthesizing zinc(II) tertiary arsine complexes of unpredictable geometries might be realised by the application of our new synthetic route.

Results and Discussion

Zinc metal powder was treated with Et_3AsI_2 in a 1:1 ratio, equation (2). The product from the reaction was initially quite

$$Et_3AsI_2 + Zn \xrightarrow[Et_2O,\ r.t.]{ca.\ 24\ h,\ N_2} [ZnI_2(AsEt_3)]_2 \qquad (2)$$

oily, but removal of the solvent and recrystallisation of the resultant solid from diethyl ether produced a large number of colourless crystals on standing at *ca.* 0 °C, and one of these was selected for analysis by single-crystal X-ray diffraction. The structure of $[ZnI_2(AsEt_3)]_2$ is revealed in Fig. 1. Selected bond lengths and angles are given in Table 1. As expected, a dimeric species results which is isostructural with the phosphine complex $[ZnI_2(PEt_3)]_2$[9] and the cadmium complex $[CdI_2$-

Table 1 Selected bond lengths (Å) and angles (°) for $[ZnI_2(AsEt_3)]_2$

I(1)–Zn(1)	2.522(3)	As(1)–Zn(1)	2.446(3)
I(2)–Zn(1)	2.681(3)		
Zn(1)–I(2)–Zn(2)	80.7(1)	I(2)–Zn(1)–I(2)	99.3(1)
I(1)–Zn(1)–I(2)	114.9(1)	I(2)–Zn(1)–As(1)	107.4(1)
I(1)–Zn(1)–As(1)	113.8(1)		

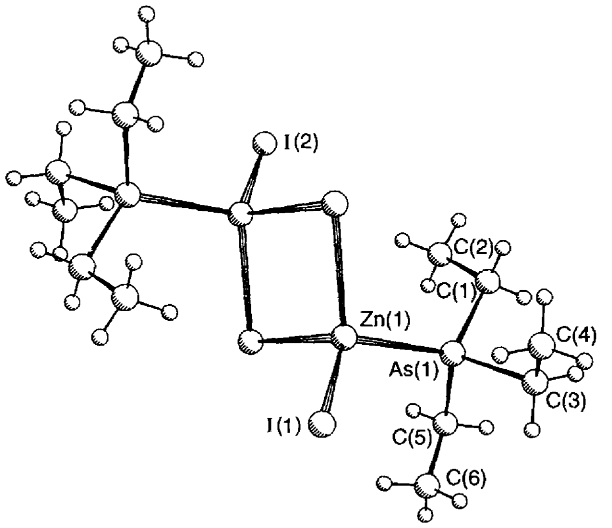

Fig. 1 Crystal structure of the dimeric complex $[ZnI_2(AsEt_3)]_2$

Table 2 Selected bond lengths (Å) and angles (°) for $ZnI_2(AsMe_3)_2$

I(1)–Zn(1)	2.545(8)	As(1)–Zn(1)	2.445(8)
I(2)–Zn(1)	2.574(8)	As(2)–Zn(1)	2.469(9)
I(3)–Zn(2)	2.574(8)	As(3)–Zn(2)	2.493(7)
I(4)–Zn(2)	2.548(8)	As(4)–Zn(2)	2.474(9)
I(1)–Zn(1)–I(2)	118.2(3)	I(3)–Zn(2)–I(4)	120.3(3)
I(1)–Zn(1)–As(1)	110.8(3)	I(3)–Zn(2)–As(3)	105.7(3)
I(1)–Zn(1)–As(2)	105.6(3)	I(3)–Zn(2)–As(4)	110.0(3)
I(2)–Zn(1)–As(2)	107.1(3)	I(4)–Zn(2)–As(3)	106.5(3)
I(2)–Zn(1)–As(1)	104.5(3)	I(4)–Zn(2)–As(4)	108.1(3)
As(1)–Zn(1)–As(2)	110.6(3)	As(3)–Zn(2)–As(4)	105.2(3)

$(AsEt_3)]_2$.[15] The yield is quantitative and no evidence for any other product, for example the bis(ligand) species $ZnI_2(AsEt_3)_2$, was observed.

On the other hand, Me_3AsI_2 reacts with zinc metal powder according to equation (3). Surprisingly, Me_3AsI_2 reacts in a

$$2Me_3AsI_2 + 2Zn \xrightarrow[Et_2O,\ r.t.]{ca.\ 1\ d,\ N_2} ZnI_2(AsMe_3)_2 + ZnI_2 \quad (3)$$

different way than does Et_3AsI_2, producing equimolar quantities of the bis(ligand) complex $ZnI_2(AsMe_3)_2$ and zinc iodide, the latter being identified by X-ray powder diffraction; a comparison of the ZnI_2 produced from this experiment and the standard data-base entry for ZnI_2 showed very good agreement. The structure of $ZnI_2(AsMe_3)_2$ is revealed in Fig. 2. Selected bond lengths and angles are given in Table 2. The reason why the reaction of Me_3AsI_2 with zinc produces a monomeric complex and that of Et_3AsI_2 produces a dimeric complex is unclear. Basicity factors are unimportant, since the basicities of Me_3As and Et_3As are virtually identical. Steric factors[16] may be important, since the cone angle of Et_3As, 134°, is appreciably larger than that of Me_3As, 121°. Adopting a dimeric structure clearly relieves steric crowding at the zinc centre since only one, rather than two, tertiary arsine ligands are co-ordinated. Although the two complexes described herein represent the only structurally characterised co-ordination compounds of zinc(II) containing a zinc–arsenic bond, there is one example of a structurally characterised organometallic compound containing such a bond, $[Bu^tZn(AsBu^t_2)]_2$, synthesized by Groshens *et al.*[17] This complex contains the zinc atoms in planar three-co-ordinate geometry. The zinc–arsenic bond in this structure is 2.506 Å, rather longer than those in the compounds described here, 2.446(3) Å for $[ZnI_2(AsEt_3)]_2$ and 2.445(8)–2.493(7) Å for $ZnI_2(AsMe_3)_2$.

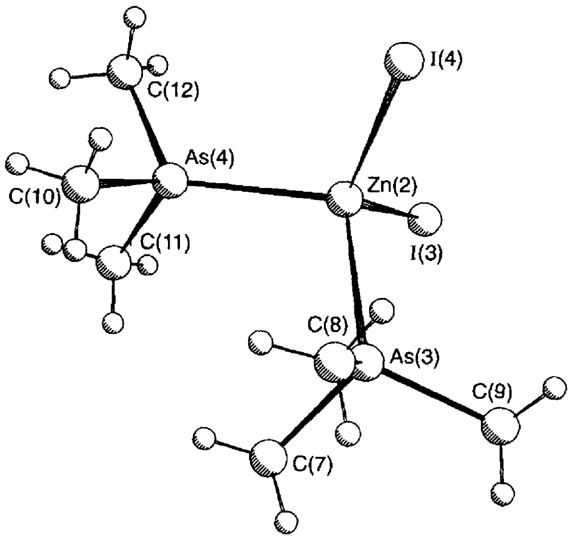

Fig. 2 Crystal structure of the monomeric complex $ZnI_2(AsMe_3)_2$ (two tetrahedral species are present in the asymmetric unit)

Conclusion

The two complexes described not only represent the first structurally characterised co-ordination compounds of zinc(II) containing tertiary arsine ligands but also exhibit an interesting structural change in the complex formed on changing the R groups on the tertiary arsine. The most probable reason for this is steric considerations. The characterisation of $ZnI_2(AsMe_3)_2$ unequivocally shows that a bis(ligand) complex of zinc(II) with a Group 15 donor ligand does exist and the assertion of Goel *et al.*[6] that analogous tertiary phosphine complexes are, in fact, mixed phosphine–phosphine oxide complexes, $ZnX_2(PR_3)(OPR_3)$, may not be correct. However, in agreement with these workers, from the results presented here it appears that the bis(ligand) complexes are restricted to ER_3 ligands (E = P or As) with very small cone angles.

Experimental

The zinc(II)–arsine complexes are moisture sensitive, as are the trialkylarsine diiodide compounds, R_3AsI_2. Therefore strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box. The synthesis and characterisation of Me_3AsI_2 has been described elsewhere.[18] The compound Et_3AsI_2 was prepared in an identical manner from the direct reaction of (redistilled) commercially available $AsEt_3$ (Strem) with I_2 in diethyl ether; standard reagent-grade coarse-grain zinc metal powder was obtained commercially and used as received. Diethyl ether (BDH) was dried over sodium wire for *ca.* 1 d and subsequently distilled over CaH_2 in an inert atmosphere (N_2).

Both complexes described were synthesized by the direct reaction of zinc metal powder with the R_3AsI_2 compound in diethyl ether. The isolation of $[ZnI_2(AsEt_3)]_2$ was straightforward, being the quantitative product from the reaction. Triethylarsine diiodine (0.73 g, 1.75 mmol) was suspended in diethyl ether (*ca.* 100 cm^3) and subsequently zinc metal powder (0.11 g, 1.75 mmol) was added. After *ca.* 24 h the resultant oily off-white solid was isolated by the removal of the diethyl ether *in vacuo*. The solid was dried *in vacuo* and transferred to pre-dried argon-filled ampoules which were flame sealed [Found (Calc.): C, 15.3 (15.0); H, 3.3 (3.1); I, 52.7 (52.8)%]. Isolation of a pure sample of $ZnI_2(AsMe_3)_2$ was problematical, since it was produced in 50% yield along with ZnI_2. The similar solubilities of these products rendered their separation difficult but careful

Table 3 Crystal data and details of refinement for $[ZnI_2(AsEt_3)]_2$ and $ZnI_2(AsMe_3)_2$

	$[ZnI_2(AsEt_3)]_2$	$ZnI_2(AsMe_3)_2$
Formula	$C_{12}H_{30}As_2I_4Zn_2$	$C_6H_{18}As_2I_2Zn$
M	962.59	559.24
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	7.789(8)	12.318(7)
b/Å	11.889(8)	15.711(5)
c/Å	14.886(5)	8.534(3)
α/°	—	90.98(2)
β/°	104.03(5)	91.07(3)
γ/°	—	93.90(3)
U/Å^3	1337(3)	1647(2)
Z	2	4
D_c/g cm^{-3}	2.390	2.255
F(000)	880	1024
μ/cm^{-1}	88.56	91.83
Crystal size/mm	0.3 × 0.3 × 0.1	0.4 × 0.3 × 0.05
Decomposition (%)	0	23
Maximum 2θ	50.2	50.0
Maximum, minimum transmissions^a	0.91, 1.06	0.74, 1.50
Total data measured	2695	5146
Number of unique reflections	2500	4549
Number of observed reflections [$I > 3.00\sigma(I)$]	1246	1379
Number of parameters	92	184
Minimum, maximum residual electron density/e Å^{-3}	−0.86, 0.82	−1.21, 1.21
Maximum least-squares shift to error ratio	0.03	0.09
g in $w = 1/[\sigma^2(F) + gF^2]$	0.03	0.03
Final *R*	0.051	0.095
Final R'^b	0.060	0.076

^{a} Absorption correction by azimuthal scan technique. ^{b} Function minimised $\Sigma w(|F_o| - |F_c|)^2$.

fractional crystallisation enabled a pure sample of $ZnI_2(AsEt_3)_2$ to be isolated. Reaction times were 1–2 d, appreciably longer than for the analogous zinc tertiary phosphine complexes, which typically formed in *ca.* 1 h.

Elemental analyses were performed by the Microanalytical Laboratory of this department. X-Ray powder diffraction patterns were recorded on a Scintag XRD2000 diffractometer using Cu-Kα radiation (λ = 1.5418 Å).

Crystallography

Crystal data and details of refinement for both structures are presented in Table 3. Colourless crystals were mounted in Lindemann tubes under an atmosphere of dry argon. All measurements were performed on a Rigaku AFC6S diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and ω–2θ scans. Both structures were solved by direct methods using SHELXS 86[19] and refined by full-matrix least squares based on *F* using TEXSAN.[20] All hydrogen atoms were constrained to chemically reasonable positions (C–H 0.95 Å) with isotropic thermal parameters set at 120% of the equivalent *B* values of the bonded atom. Neutral atom scattering factors were used throughout. The high final residuals for the complex $ZnI_2(AsMe_3)_2$ are due to significant decomposition of the crystal during data collection (see Table 3).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/126.

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