Stabilisation of Copper(II) Tertiary-phosphine or -arsine Complexes. Part 1. Complexes of Copper(II) with Hybrid Oxygen–Arsenic Ligands from *o*- and *p*-(Diphenylarsino)benzoic Acids

Swarn S. Parmar,* Tejpal S. Basra, and Sarjit S. Sandhu
Department of Chemistry, Guru Nanak Dev University, Amritsar, India

---

Oxygen–arsenic hybrid ligands from *o*- and *p*-(diphenylarsino)benzoic acids have been used to prepare 20 stable copper(II)–arsine complexes which have been characterised with the help of elemental analysis, t.g.a. (thermal gravimetric analysis), d.t.a. (differential thermal analysis), room temperature magnetic susceptibility, i.r. and u.v.-visible spectral data. An attempt has been made to explain the earlier failures to prepare such complexes, which invariably led to the formation of either copper(I)–arsine or copper(II)–arsine oxide complexes.

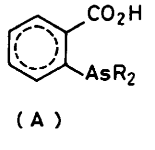
All earlier attempts [1–8] to obtain copper(II)–arsine complexes of tertiary arsines invariably yielded either a copper(I)–arsine or a copper(II)–arsine oxide complex owing to the rapid reduction of copper(II) to copper(I) and simultaneous oxidation of the arsine to arsine oxide. It was only in 1968 that we prepared two copper(II)–arsine complexes, [Cu(*o*-dpab)$_2$] and [Cu(*o*-dtab)$_2$] by reacting copper(II) acetate monohydrate with *o*-(diphenylarsino)benzoic acid (*o*-Hdpab) (A; R = Ph) and *o*-[di(*p*-tolyl)arsino]benzoic acid (*o*-Hdtab) (A; R = *p*-tolyl), while under similar conditions their methyl analogue, (A; R = Me), afforded only a copper(I)–arsine complex.[9] Subsequent attempts [10–15] yielded only four copper(II)–arsine complexes; [Cu(hfacac)$_2$(AsPh$_3$)$_n$] (hfacac = hexafluoroacetylacetonate; *n* = 1 or 2) [13] and [Cu(*o*-H$_2$NC$_6$H$_4$AsR$_2$)$_2$(ClO$_4$)$_2$] (R = Me or Ph).[14] In continuance, we now report the preparation and probable structures of twenty such complexes using the hybrid oxygen–arsenic ligands *o*-Hdpab and *p*-Hdpab in order to determine the factors responsible for their stability.

Experimental

Copper(II) was estimated by ethylenediaminetetra-acetic acid, using xylenol orange as indicator.[16] For arsenic(III), the copper(II) complex (0.05 g) was dissolved in a minimum amount of boiling glacial acetic acid. Distilled water was added until turbidity appeared which was removed by adding a few drops of dilute acetic acid. The resulting clear solution was then titrated against 0.02 N iodine solution. The arsenic(III) could not be estimated accurately in the aniline adducts due to the dark brown colour of this solution. Details of other physical measurements are the same as described earlier.[17]

The ligands *o*-Hdpab and *p*-Hdpab were prepared from the corresponding isomer of (dichloroarsino)benzoic acid.[18] Other ligand abbreviations employed include: py (pyridine), quin (quinoline), α-, β-, γ-pic (picoline), an (aniline), and diox (1,4-dioxan).

Preparations.—[Cu(*o*-dpab)$_2$]·H$_2$O (*brown*) *and* [Cu(*o*-dpab)$_2$(H$_2$O)]·H$_2$O (*blue-green*). The addition of a methanolic solution (25 cm^3) of *o*-Hdpab (3.5 g, 10 mmol) to a methanolic solution (50 cm^3) of copper(II) acetate monohydrate (1.0 g, 5 mmol) gave a brown solid which was filtered off, washed with methanol, and dried *in vacuo*. In another experiment, the brown solid was not filtered but stirred (1 h) which changed its colour to blue-green. This product was filtered off, washed with methanol, and dried *in vacuo*. The filtrate, on refluxing, gave a yellow compound which could not be characterised with certainty.



(A)

[Cu(*o*-dpab)$_2$]·H$_2$O (*dark green*) *and* [Cu(*o*-dpab)$_2$(H$_2$O)$_2$]·H$_2$O (*light green*). The addition of an ethanolic solution (15 cm^3) of *o*-Hdpab (3.5 g, 10 mmol) to an ethanolic solution (50 cm^3) of copper(II) acetate monohydrate (1.0 g, 5 mmol) gave a brown solid which was found to be identical with the brown compound obtained from methanol and n-propanol. In an alternative experiment, stirring the brown solid in ethanol (1 h) afforded a dark green solid which was filtered off, washed with ethanol, and dried *in vacuo*.

On refluxing the dark green filtrate of the above reaction mixture for 1 h, a light green solid was obtained. This was found to be the same as that obtained by refluxing for 1 h a reaction mixture containing a suspension of copper(II) acetate monohydrate (2.1 g, 3 mmol) in 95% ethanol (30 cm^3) and a solution of *o*-Hdpab (2.1 g, 6 mmol) in 95% ethanol (15 cm^3). This, however, has earlier been considered to be [Cu(*o*-dpab)$_2$] on the basis of estimation of copper(II) and arsenic(III) alone.[9]

[Cu(*o*-dpab)$_2$(H$_2$O)]·H$_2$O (*brown-green*). The addition of copper(II) acetate monohydrate (1.0 g, 5 mmol) to a solution of *o*-Hdpab (3.5 g, 10 mmol) in acetone (75 cm^3) gave a brown solution on shaking, which on refluxing for 2 h afforded a brown-green solid. This was filtered off, washed with acetone, and dried *in vacuo*.

[Cu(*p*-dpab)$_2$(H$_2$O)$_2$] (*blue*). A suspension of copper(II) acetate monohydrate (0.6 g, 3 mmol) and a solution of *p*-Hdpab (2.1 g, 6.0 mmol) in 95% ethanol (45 cm^3) yielded a blue complex on refluxing for 3 h which was washed with the same solvent and dried *in vacuo*.

[Cu(*o*-dpab)$_2$L$_2$] (L = py, quin, α-pic, β-pic, *or* γ-pic), [Cu(*o*-dpab)$_2$(an)], *and* [Cu(*o*-dpab)$_2$(diox)(H$_2$O)]. Boiling the mixture containing a solution of *o*-Hdpab (3.5 g, 10 mmol) in hot acetone (10 cm^3) with a suspension of copper(II) acetate monohydrate (1.0 g, 5 mmol) in acetone (40 cm^3) under reflux in the presence of the base (10 cm^3) yielded a solid product, which was filtered off, washed with acetone, and dried *in vacuo*.

[Cu(*p*-dpab)$_2$L$_n$] [L = py *or* γ-pic (*n* = 2); an, β-pic, *or* quin (*n* = 1)], [Cu(*p*-dpab)$_2$(diox)$_2$]·H$_2$O, *and* [Cu(*p*-dpab)$_2$(α-pic)(H$_2$O)]. Here the medium of reaction mixture was 95% ethanol while the method of preparation was the same as used in the case of reactions of the *ortho* isomer.

Table 1. Elemental and thermal data of complexes of copper(II) with *o*-Hdpab and *p*-Hdpab

		Analysis [a] (%)					Thermal analysis				
Compound	M.p./ °C	C	H	N	Cu	As^{III}	Decomp. stage	Temp. range/°C	Stepwise loss (%)	Calc. loss (%)	d.t.a peak temp. range/ [b] °C
$[Cu(o\text{-}dpab)_2]\cdot H_2O$	180	58.55	4.00		8.10	19.00	I	55—140	2.3	2.31 (H_2O)	140
(brown)		(58.50)	(3.85)		(8.15)	(19.25)					
$[Cu(o\text{-}dpab)_2]\cdot H_2O$	188	57.95	3.75		7.65	19.50	I	50—160	2.6	2.31 (H_2O)	140 (sh)
(dark green)		(58.50)	(3.25)		(8.15)	(19.25)					160
$[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$	186	57.70	3.95		8.35	18.80	I	60—125	2.30	2.26 (H_2O)	90
(blue-green)		(57.20)	(4.00)		(7.95)	(18.80)	II	125—180	2.37	2.26 (H_2O)	140
$[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$	189	57.50	3.70		8.25	18.00	I	80—160	2.56	2.26 (H_2O)	140
(brown-green)		(57.20)	(4.00)		(7.95)	(18.80)	II	180—200	2.56	2.26 (H_2O)	180
$[Cu(o\text{-}dpab)_2(H_2O)_2]\cdot H_2O$	198	56.55	4.30		8.90	17.65	I	80—145	2.30	2.20 (H_2O)	120
(light green)		(55.90)	(4.15)		(7.80)	(18.50)	II	145—165	2.70	2.20 (H_2O)	170
							III	175—200	2.50	2.20 (H_2O)	
$[Cu(p\text{-}dpab)_2(H_2O)_2]$	248	57.40	3.90		7.95	19.15	I	50—110	2.50	2.26 (H_2O)	75, 155
(blue)		(57.20)	(4.00)		(7.95)	(18.90)	II	110—170	2.01	2.26 (H_2O)	
$[Cu(o\text{-}dpab)_2(py)_2]$	186	62.50	4.15	2.80	5.85	16.15	I	Up to 200	No loss	*c*	150
(violet)		(62.65)	(4.15)	(3.05)	(6.90)	(16.30)	II	220—265	8.4	8.6 (py)	220
							III	265—280	8.0	8.6 (py)	300
$[Cu(o\text{-}dpab)_2(quin)_2]$	183	65.10	4.20	2.80	6.20	13.90	I	Up to 200	No loss	*c*	160
(dirty blue)		(65.90)	(4.10)	(2.75)	(6.10)	(14.40)	II	200—260	25.0	25.3 (2 quin)	240—360
$[Cu(o\text{-}dpab)_2(\alpha\text{-}pic)_2]$	190	63.65	4.70	3.10	5.75	14.65	I	Up to 200	No loss	*c*	140
(pink)		(63.60)	(4.45)	(2.95)	(6.70)	(15.85)	II	200—280	18.27	19.63 (2 α-pic)	280
$[Cu(o\text{-}dpab)_2(\beta\text{-}pic)_2]$	184	63.10	4.85	2.85	6.10	15.00	I	Up to 200	No loss	*c*	110, 160
(light blue)		(63.30)	(4.45)	(2.95)	(6.70)	(15.85)	II	200—255	19.5	19.65 (2 β-pic)	230
$[Cu(o\text{-}dpab)_2(\gamma\text{-}pic)_2]$	195	63.00	4.70	3.35	6.15	15.00	I	Up to 180	No loss	*c*	160
(dark blue)		(63.30)	(4.45)	(2.95)	(6.70)	(15.85)	II	185—250	19.10	19.65 (2 γ-pic)	160
$[Cu(o\text{-}dpab)_2(an)]$	235	61.60	4.15	2.00	7.95		I	60—220	9.4	10.88 (an)	210
(black)		(61.80)	(4.45)	(1.65)	(7.85)						
$[Cu(o\text{-}dpab)_2(diox)(H_2O)]$	191	58.10	4.30		6.35	17.65	I	80—120	1 74	2.97 (H_2O)	160
(green)		(58.10)	(4.40)		(7.30)	(17.30)					
$[Cu(p\text{-}dpab)_2(py)_2]$	262	61.05	4.20	2.90	7.30	16.90	I	Up to 120	No loss	*c*	170
(bright blue)		(62.25)	(4.15)	(3.05)	(6.90)	(16.30)	II	120—180	8.50 (fast)	8.6 (py)	165, 190
							III	180—290	8.50 (slow)	8.6 (py)	
$[Cu(p\text{-}dpab)_2(quin)]$	246	63.00	4.15	1.05	7.00	16.90	I	Up to 120	No loss	*c*	120
(blue)		(63.50)	(3.95)	(1.55)	(7.15)	(16.85)	II	120—220	14.5	14.49 (quin)	165
$[Cu(p\text{-}dpab)_2(\alpha\text{-}pic)(H_2O)]$	245	60.70	4.20	1.65	8.05	16.50	I	40—120	3.20	2.06 (H_2O)	120
(green)		(60.60)	(4.25)	(1.60)	(7.20)	(17.20)	II	220—270	10.31	10.66 (α-pic)	195, 260
$[Cu(p\text{-}dpab)_2(\beta\text{-}pic)]$	242	62.40	4.35	1.65	7.35	17.25	I	Up to 180	No loss	*c*	120
(violet blue)		(61.80)	(4.10)	(1.65)	(7.45)	(17.55)	II	180—295	11.00	10.88 (β-pic)	220
$[Cu(p\text{-}dpab)_2(\gamma\text{-}pic)_2]$	246	62.65	4.50	2.85	7.15	15.40	I	Up to 180	No loss	*c*	220
(green)		(63.30)	(4.45)	(2.95)	(6.70)	(15.85)	II	180—260	10.9	10.88 (γ-pic)	200
							III	260—320	10.81	10.88 (γ-pic)	290
$[Cu(p\text{-}dpab)_2(an)]$	300	60.70	4.00	4.00	8.00		I	80—240	10.88	10.88 (an)	230 [d]
(black)		(61.80)	(4.10)	(1.65)	(7.45)						270
		(63.30) [e]	(4.45) [e]	(2.95) [e]	(6.70) [e]						
$[Cu(p\text{-}dpab)_2(diox)_2]\cdot H_2O$	232	57.90	4.80		7.15	15.40	I	40—100	1.68	1.92 (H_2O)	120
(blue-green)		(57.80)	(4.70)		(6.65)	(15.70)	II	120—305	18.78	18.78(2 diox)	300

[a] Calculated values in parentheses. [b] Endothermic unless otherwise stated. [c] Conformation change. [d] Exothermic. [e] Calculated values are for $[Cu(p\text{-}dpab)_2(an)_2]$; N(%) favours $[Cu(p\text{-}dpab)_2(an)_2]$, but C(%) together with the rest of the data are similar to those of $[Cu(o\text{-}dpab)_2(an)]$ and favour the formula $[Cu(p\text{-}dpab)_2(an)]$.

Results and Discussion

The presence of water in the hydrated complexes is supported by the appearance of i.r. bands due to ν(OH) and δ(HOH) at 3 240—3 500 and 1 600—1 640 cm^{-1} respectively.[19] A band at 820, 820, 837, and 840 cm^{-1} observed successively in the i.r. spectra of the aqua complexes, $[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (blue-green and brown-green isomers), $[Cu(o\text{-}dpab)_2(H_2O)_2]\cdot H_2O$ (light green), and $[Cu(p\text{-}dpab)_2(H_2O)_2]$ (blue), in addition to a δ(OCO) band at 840—860 cm^{-1} may be assigned to the ρ(H_2O) of the co-ordinated water.[20] Bands other than δ(OCO) present in the range 800—900 cm^{-1} of the i.r. spectra of the base adducts are characteristic of the respective bases.[19,21—24]

The thermal gravimetric analysis (t.g.a.) data (Table 1) show that the hydrated complexes start losing lattice water

Table 2. Infrared, reflectance spectra (cm^{-1}), molar conductance, and magnetic moment data of complexes of copper(II) with *o*-Hdpab and *p*-Hdpab

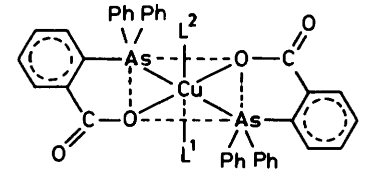
Complex	H_2O bands $\nu(OH)$ [$\delta(HOH)$]	CO_2 bands $\nu_{asym}(CO_2)$, $\nu_{sym}(CO)_2$	Reflectance spectra [a]/ *d–d*, c.t. bands	$\mu_{eff.}$[b]/ B.M.	Λ/S cm^{-2} mol^{-1} (CH_2Cl_2)	(Structure; stereochemistry) [c]
Na(*o*-dpab)		1 595vs, 1 400vs				
$[Cu(o\text{-}dpab)_2(py)_2]$		1 585ms, 1 365vs	14 286, 16 667	1.80	11.32	(B; doct)
$[Cu(o\text{-}dpab)_2(quin)_2]$		1 593ms, 1 370vs	13 514 (sh), 16 949	2.00	6.84	
$[Cu(o\text{-}dpab)_2(\alpha\text{-}pic)_2]$		1 607s, 1 364vs	14 286, 17 857	2.10	6.58	
$[Cu(o\text{-}dpab)_2(\beta\text{-}pic)_2]$		1 590vs, 1 360vs 1 575s	13 514 (sh), 14 286 (sh), 16 393	2:00	6.05	
$[Cu(o\text{-}dpab)_2(\gamma\text{-}pic)_2]$		1 595vs, 1 369vs	13 158 (sh), 14 286, 16 667	2.00	6.84	
$[Cu(o\text{-}dpab)_2(diox)(H_2O)]$	3 458 (br)	1 615vs, 1 410vs	14 085	1.73	3.03	
$[Cu(o\text{-}dpab)_2(an)]$		1 623vs, 1 383 1 373 [d]	12 987, 15 152 (sh), 20 000 [e]	2.00	5.00	(B; spy, L¹ missing)
$[Cu(o\text{-}dpab)_2]\cdot H_2O$ (brown)	3 405 (br), [1 623 (br)]	1 623 (br), 1 380 (br), 1 600 (br), 1 403 (br)	10 632 (sh), 13 423	1.78	1.84	(C/D; ctet)
$[Cu(o\text{-}dpab)_2]\cdot H_2O$ (dark green)	3 395 (br), [16 623 (br)]	1 623 (br), 1 380s, 1 600vs, 1 403s (br)	12 821 (sh), 15 626, 21 739 [e]	2.33	1.97	
$[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (blue-green)	3 350s (br), [1 623 (sh)]	1 613vs, 1 415vs	14 710	1.52	1.92	(E; doct)
$[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (brown-green)	3 225s (br), [1 625 (sh)]	1 600vs,[d] 1 405vs, 1 625 (sh), 1 370 (sh)	13 889 (sh), 17 857, 21 740 [e]	1.92	2.92	(F; spy)
$[Cu(o\text{-}dpab)_2(H_2O)_2]\cdot H_2O$ (light green)	3 388 (br), [1 635 (sh)]	1 625s, 1 378vs, 1 612s, 1 345m	11 490	1.64	1.23	(G; doct)
Na(*p*-dpab)		1 595vs, 1 400vs				
$[Cu(p\text{-}dpab)_2(H_2O)_2]$ (blue)	3 526 (sh) [1 640 (sh)]	1 604vs (br), 1 404vs	13 514	1.93	2.44	(H; doct)
$[Cu(p\text{-}dpab)_2(py)_2]$		1 600vs, 1 382vs	10 870 (sh), 15 152	1.96	0.68	
$[Cu(p\text{-}dpab)_2(\gamma\text{-}pic)_2]$		1 595vs, 1 369vs	13 889 (sh), 16 667	1.85	1.18	
$[Cu(p\text{-}dpab)_2(\alpha\text{-}pic)(H_2O)]$		1 620vs, 1 400vs	12 903 (sh)	1.87	0.26	
$[Cu(p\text{-}dpab)_2(diox)_2]\cdot H_2O$		1 610vs, 1 405vs	10 204 (sh), 14 180	1.87	1.89	
$[Cu(p\text{-}dpab)_2(quin)]$		1 620vs, 1 404vs	12 500	1.81	0.21	(H; doct, L¹ missing, CO_2 – bridging)
$[Cu(p\text{-}dpab)_2(\beta\text{-}pic)]$		1 620vs, 1 400vs	13 072	1.86	0.66	
$[Cu(p\text{-}dpab)_2(an)]$		1 585s, 1 385ms	13 793s, 19 231 [e]	2.33	0.61	

[a] *d–d* Bands unless otherwise stated. [b] 1 B.M. = 0.927×10^{-23} A m². [c] doct = Distorted octahedron, spy = square pyramid, ctet = compressed tetrahedron. [d] Strong doublet. [e] Charge transfer (c.t.) band.

below 100 °C while the remaining water molecules, if any, may be regarded as co-ordinated.[25] The differential thermal analysis (d.t.a.) curves of all the adducts except $[Cu(o\text{-}dpab)_2L]$ [L = (an), or (diox)(H_2O)] and $[Cu(p\text{-}dpab)_2L]$ [L = (α-pic)(H_2O), (an), or $(diox)_2(H_2O)$] contain an endothermic peak at 160—180 °C whereas the corresponding t.g.a. curves show no loss, indicating that some type of conformational change takes place before the loss of base molecules. The t.g.a. curve of the compound, considered to be $[Cu(o\text{-}dpab)_2(diox)(H_2O)]$ on the basis of elemental analysis, indicates the loss of only half a molecule of 1,4-dioxan, which is surprising.

The i.r. spectra of $[Cu(o\text{-}dpab)_2]\cdot H_2O$ (brown and dark green), $[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (brown-green), and $[Cu(o\text{-}dpab)_2(H_2O)_2]\cdot H_2O$ (light green) complexes show the splitting of both the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands indicating the presence of more than one bonding mode of the carboxylate ion.[26–32] In the case of all the remaining complexes except the aniline adducts and $[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (blue-green), only one of the two carboxylate bands suffers an appreciable change relative to those of the ligand sodium salt.

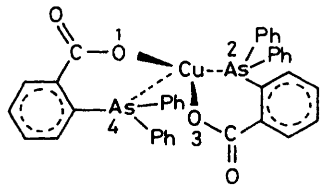
Table 2 shows that only the blue-green $[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ and light green $[Cu(o\text{-}dpab)_2(H_2O)_2]\cdot H_2O$ complexes possess subnormal room-temperature $\mu_{eff.}$ values. The reflectance spectral data (Table 2) of these complexes show that only $[Cu(o\text{-}dpab)_2(an)]$ (dark brown), $[Cu(p\text{-}dpab)_2(an)]$ (dark brown), $[Cu(o\text{-}dpab)_2]\cdot H_2O$ (brown and dark green), and $[Cu(o\text{-}dpab)_2(H_2O)]\cdot H_2O$ (brown-green) possess a low-energy charge transfer band at 19 000—22 000 cm^{-1} in addition to broad *d–d* bands which are the only feature of the rest of the complexes.



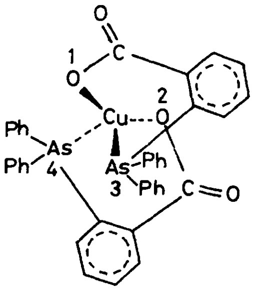
(B)

The spectral data [26,33] together with the non-electrolytic nature in dichloromethane can be explained if the structures (B)—(H) are assigned to these complexes as indicated in Table 2. The complexes with *d–d* bands alone have been assumed to be distorted octahedral and in some of these a large distortion gives rise to the appearance of more than one band.

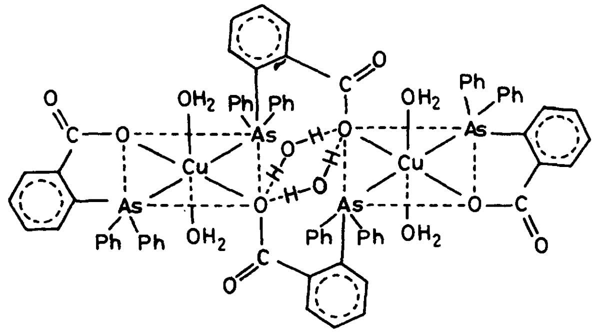
The preceding discussion reveals that all the structures proposed for copper(II) complexes indicate co-ordination of



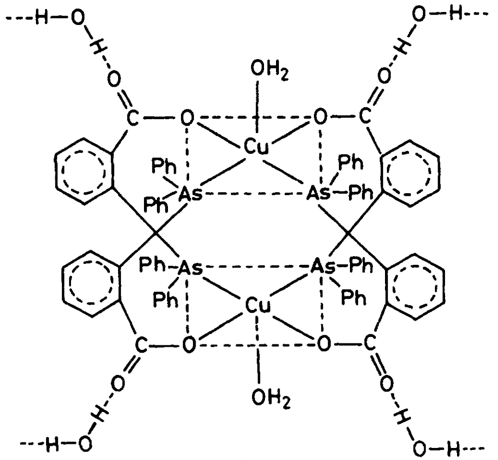
(C)



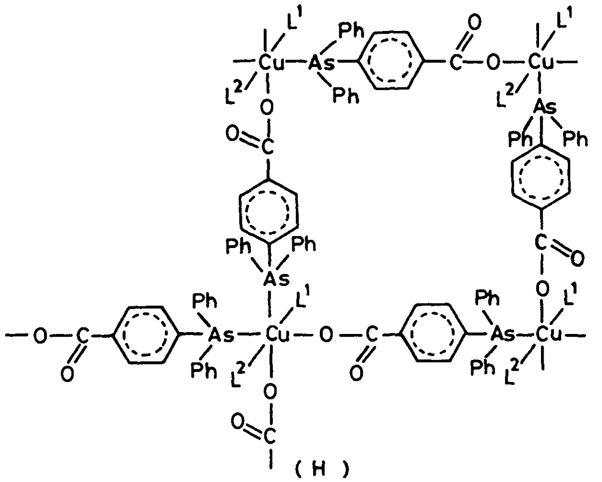
(D)



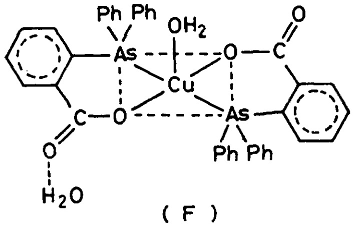
(G)



(E)



(H)



(F)

arsenic(III). The reported magnitude of the shift (5—10 cm^{-1}) of the ν(As–C)(aromatic) band of the ligand on co-ordination through arsenic(III) is so small that a slight error in the standardisation of the i.r. may lead to incorrect conclusions and has not been found to be useful.

Earlier workers who failed to stabilise copper(II)–arsine complexes used monotertiary arsines in the form of unidentate ligands which reduce a part of copper(II) to copper(I) and yield an equivalent amount of the corresponding arsine oxide. In accordance with the hard/soft acid and base principle, the soft acceptor copper(I) prefers to bond with the soft donor arsenic(III) while the borderline acid copper(II) is left to bond only with the hard oxygen of the arsine oxide leading to the formation of either a copper(I)–arsine or a copper(II)–arsine oxide complex.

The stabilisation of the arsenic(III)–copper(II) bond in the chelates of the anion *o*-dpab may be attributed to the formation of a stable six-membered unsaturated chelate ring which appears to precede the reduction of copper(II) to copper(I) and forces the borderline acid copper(II) to behave as soft. The observed stabilisation of the arsenic(III)–copper(II) bonds in the complexes of the non-chelating anion *p*-dpab may be due to the formation of a highly cross-linked structure (H).

The formation of [Cu(*o*-$H_2NC_6H_4AsR_2$)$(ClO_4)_2$] where R = Ph (at room temperature) and where R = Me (at −20 °C) as well as the high stability of the former over the latter reflect the influence of the inductive effect of the substituent on arsenic(III). Both these complexes are stabilised by the chelate effect provided chelation takes precedence over the reduction of copper(II).

Thus all the copper(II)–arsine complexes except [Cu(hfacac)$_2$($AsPh_3$)$_n$] have been stabilised by means of hybrid oxygen-arsenic or nitrogen-arsenic ligands.[13]

The results of the present investigation support the conclusion made by Kato *et al.*[34] that the correlation of the type of copper(II) complex formed with the basic properties of the solvent is a complicated problem since slight change in the reaction conditions (*e.g.* temperature and time) yields different products.

References

1 R. S. Nyholm, *J. Chem. Soc.*, 1951, 1767 and refs. therein.
2 A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 1951, 38.
3 W. Cochran, F. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 1957, 2816.
4 B. Chiswell and S. E. Livingstone, *J. Chem. Soc.*, 1959, 2931.
5 H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, 1959, **81**, 311.
6 B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.*, 1961, **23**, 327.
7 G. A. Barclay, C. M. Harris, and J. V. Kingston, *Chem. Ind.* (*London*), 1965, 227.
8 R. D. Feltham, H. G. Metzger, and W. Silverthorn, *Inorg. Chem.*, 1968, **7**, 2003.
9 S. S. Sandhu and S. S. Parmar, *Chem. Commun.*, 1968, 1335.

10 H. A. Tayim, A. Bouldoukian, and F. Awad, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3799.

11 F. H. Jardine and F. J. Young, *J. Chem. Soc. A*, 1971, 2444.

12 F. H. Jardine, A. C. Vohra, and F. J. Young, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2941.

13 R. A. Zelonka and M. C. Baird, *Chem. Commun.*, 1971, 780; *Can. J. Chem.*, 1972, **50**, 1269.

14 B. Chiswell, R. A. Plowmann, and K. Verrall, *Inorg. Chim. Acta*, 1972, **6**, 113.

15 H. J. Gysling, *Inorg. Synth.*, 1979, **19**, 92.

16 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., ELBS and Longman, London, 1973, p. 443.

17 S. S. Parmar and H. Kaur, *Transition Met. Chem.*, 1982, **7**, 79.

18 S. S. Sandhu and S. S. Parmar, *Z. Anorg. Allg. Chem.*, 1968, **363**, 207.

19 K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, London, 1970, p. 150.

20 M. D. Taylor, C. D. Carter, and C. I. Wynter, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1503.

21 T. J. Delie, M. A. Little, and D. X. West, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1400.

22 M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, 1965, **21**, 105.

23 N. S. Gill, R. H. Nuttall, D. E. Scaiff, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.

24 D. G. Brewer, P. T. T. Wong, and M. C. Scars, *Can. J. Chem.*, 1968, **46**, 3137.

25 K. Nagase, K. Sato, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 868 and refs. therein.

26 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291 and refs. therein.

27 N. W. Alcock, V. M. Tracy, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1976, 2243.

28 W. B. Bragg and G. T. Morgan, *Proc. R. Soc. London, Ser. A*, 1923, **104**, 437.

29 N. M. Karayannis, C. M. Mikulski, M. J. Stocko, L. L. Pytlewski, and M. M. Labes, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3185.

30 A. N. Speca, L. S. Gelfand, L. L. Pytlewski, C. Owens, and N. M. Karayannis, *Inorg. Chem.*, 1976, **15**, 1493.

31 L. S. Gelfand, L. L. Pytlewski, D. L. Cosgrove, C. M. Mikulski, A. N. Speca, and N. M. Karayannis, *Inorg. Chim. Acta*, 1979, **32**, 59 and refs. therein.

32 C. A. McAuliffe and W. D. Perry, *J. Chem. Soc. A*, 1969, 634.

33 B. J. Hathaway, *Struct. Bonding (Berlin)*, 1973, **14**, 49 and refs. therein.

34 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

Received 18*th August* 1981; *Paper* 1/1334