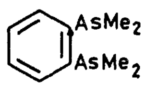
Complexes of Nickel(II) with 2,2′-Bis(dimethylarsino)biphenyl. Four-, Five-, and Six-co-ordinate Systems

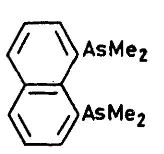
By **David W. Allen,*** **Donald F. Ashford,** and **David Hogarth,** Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB
Frederick G. Mann, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

The chelating diarsine 2,2′-bis(dimethylarsino)biphenyl (dmab) forms a series of complexes with Ni^{II} of composition [NiX$_2$(dmab)$_2$] (X = Cl, Br, I, or NCS) which are assigned a pseudo-octahedral structure on the basis of spectroscopic and magnetic-moment data. In solution in organic solvents the complexes dissociate to varying extents to form five-co-ordinate species. In addition, a series of diamagnetic five-co-ordinate complexes of composition [NiX(dmab)$_2$][ClO$_4$] (X = Cl, Br, or I) have been prepared, and are assigned a trigonal-bipyramidal structure on the basis of electronic spectra. The diarsine also forms a diamagnetic square-planar complex [Ni(dmab)$_2$][ClO$_4$]$_2$ which on treatment with iodide ion is converted into the five-co-ordinate [NiI(dmab)$_2$][ClO$_4$].

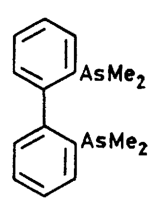
THE diarsines (1)—(3) comprise a series of chelating ligands of considerable interest in that they give the opportunity of observing the effect of increasing chelate ring size on the donor properties of the ligand and the type of complex formed with a given transition metal.



(1)



(2)



(3)

The co-ordination chemistry of *o*-phenylenebis(dimethylarsine) (1, pdma), which forms a five-membered chelate ring with a metal ion, has been extensively studied.[1] Complexes of 1,8-bis(dimethylarsino)naphthalene (2, dman) with Ni^{II}, Pd^{II}, and Pt^{II} in which the metal forms part of a six-membered ring have also been described.[2,3] However, the co-ordination chemistry of 2,2′-bis(dimethylarsino)biphenyl (3, dmab)[4] has not been investigated. Metal complexes of (3) are of interest in that the metal is part of a seven-membered chelate-ring system, of which there are relatively few examples. In addition, such chelate complexes are dissymmetric due to the presence of the 2,2′-disubstituted biphenyl unit and are thus theoretically capable of resolution into optically active forms. Such complexes therefore may be of interest in connection with the homogeneous catalysis of reactions leading to the synthesis of optically active organic compounds, currently a very active field of research.[5]

We have investigated the complexes formed by (3) with Ni^{II} and now report that this diarsine is unusual in that it forms a series of pseudo-octahedral complexes of the type [NiX$_2$(dmab)$_2$] (X = Cl, Br, I, or NCS); such pseudo-octahedral complexes of Ni^{II} with diarsines are rare. The known examples are [NiX$_2${*o*-C$_6$F$_4$(AsMe$_2$)$_2$}$_2$],[6] [NiX$_2${PhMeAs(CH$_2$)$_3$AsMePh}],[7] [{NiI$_2$[SbPh$_2$(C$_6$H$_4$PPh$_2$-*o*)]}$_n$],[8] and possibly [{NiCl$_2$(*cis*-Me$_2$AsCH=CHAsMe$_2$)}$_n$].[9] In addition, we have also isolated a series of low-spin five-co-ordinate complexes of the type [NiX(dmab)$_2$][ClO$_4$] (X = Cl, Br, or I) and a four-co-ordinate (square-planar) complex [Ni(dmab)$_2$][ClO$_4$]$_2$.

RESULTS AND DISCUSSION

Addition of (3) (2 mol) in hot ethanol to a solution of the nickel(II) halide or thiocyanate (1 mol), also in ethanol, resulted in the formation of an intensely coloured solution from which green crystals of the complexes [NiX$_2$(dmab)$_2$] (X = Cl, Br, I, or NCS) separated on cooling. The same complexes were formed when (3) and the nickel(II) salt were similarly mixed in a 1 : 1 mol ratio. All of the complexes are paramagnetic, with magnetic moments indicating the presence in each of two unpaired electrons in a tetragonally distorted octahedral environment.

The solid-state (diffuse-reflectance) electronic spectra of the complexes are all similar (see Table 1) and are consistent with a pseudo-octahedral stereochemistry at nickel according to the criteria outlined by Manch and Fernelius,[10] following the work of Jørgensen.[11] Thus octahedral nickel(II) complexes exhibit absorption bands in the following regions: 8 000—12 000 (ν_1; $^3T_{2g}\leftarrow{}^3A_{2g}$); 12 000—13 000 ($\nu_2$; $^1E_g\leftarrow{}^3A_{2g}$); 15 000—19 000 [$\nu_3$; $^3T_{1g}(F)\leftarrow{}^3A_{2g}$], and 25 000—29 000 cm^{-1} [ν_4; $^3T_1(P)\leftarrow{}^3A_{2g}$]. Of these, ν_1, ν_3, and ν_4 are spin-allowed, whereas ν_2 is spin-forbidden. In consequence, ν_2 is generally a very weak absorption and may not be observed. Inspection of the present solid-state spectral data shows that for the chloro-, bromo-, and iodo-complexes, all the

---

[1] E. C. Alyea in ' Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, MacMillan, 1973, p. 329 and refs. therein.

[2] L. Di Sipio, L. Sindellari, E. Tondello, G. De Michelis, and L. Oleari, *Co-ordination Chem. Rev.*, 1967, **2**, 129.

[3] R. Ros and E. Tondello, *J. Inorg. Nuclear Chem.*, 1971, **33**, 245.

[4] M. H. Forbes, D. M. Heinekey, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1961, 2762.

[5] See, for example, R. Glaser, S. Geresh, and J. Blumenfeld, *J. Organometallic Chem.*, 1976, **112**, 355 and refs. therein.

[6] N. V. Duffy, A. J. Layton, R. S. Nyholm, D. Powell, and M. L. Tobe, *Nature*, 1966, **212**, 177.

[7] W. Levason, C. A. McAuliffe, and S. G. Murray, *Inorg. Chim. Acta*, 1977, in the press.

[8] W. Levason, C. A. McAuliffe, and S. M. Nelson, *Inorg. Chim. Acta*, 1976, **18**, L5.

[9] M. A. Bennett and J. D. Wild, *J. Chem. Soc.* (*A*), 1971, 536.

[10] W. C. Manch and W. C. Fernelius, *J. Chem. Educ.*, 1961, **38**, 192; see also, T. M. Dunn, in ' Modern Co-ordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.

[11] C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

four transitions are observed, moving to lower wavenumber from Cl to Br to I as expected in accordance with the spectrochemical series. For each of the halogeno-complexes the ratio $\nu_3 : \nu_1$ is within the range 1.6—1.8 : 1 as is generally found for octahedral nickel(II) complexes.[10] In addition, the relative intensities of the absorption bands are in keeping with those generally observed in the crystal-field spectra of such complexes, and thus their assignment as crystal-field and not charge-transfer (c.t.) bands would seem reasonable. Indeed, the complexes exhibit intense c.t. and ligand absorption bands at wavenumbers above 28 000 cm^{-1}. However, it is appreciated that the above interpretation neglects effects on the spectra arising from the possible presence of geometrical isomers of such octahedral molecules and also that the ligands in this series are markedly different from those for which the above spectroscopic correlation [10] was established.

TABLE 1

Complexes of 2,2′-bis(dimethylarsino)biphenyl (dmab) with nickel(II) halides and thiocyanate: solid-state data

Complex	Colour	μ * B.M.	Diffuse-reflectance spectra	
			$\tilde{\nu}_{max.}$/cm^{-1}	Relative intensity
[NiCl$_2$(dmab)$_2$]	Green	3.2	26 450 (ν_4)	3.0
			16 250 (ν_3)	1.0
			12 450 (ν_2)	1.7
			9 650 (ν_1)	5.1
[NiBr$_2$(dmab)$_2$]	Green	3.2	25 575 (ν_4)	2.0
			16 000 (ν_3)	1.0
			12 400 (ν_2)	1.4
			9 450 (ν_1)	3.7
[NiI$_2$(dmab)$_2$]	Olive green	3.3	23 250 (ν_4)	1.7
			15 875 (ν_3)	1.0
			12 200 (ν_2)	1.1
			9 300 (ν_1)	2.8
[Ni(NCS)$_2$(dmab)$_2$]	Grey-green	3.6	25 250 (ν_4)	2.1
			17 750 (ν_3)	1.0
			11 300 ($\nu_1 + \nu_2$)	4.1

* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

In the case of the thiocyanato-complex, ν_1 and ν_2 are not observed separately, the spectrum exhibiting a broad band centred at 11 300 cm^{-1}; ν_3 and ν_4 occur at 17 750 and 25 250 cm^{-1}. The positions of ν_4 and ν_3 relative to the position of these bands in the halogeno-complexes suggests that co-ordination to the metal involves nitrogen-bonded thiocyanate. Evidence in support of this is obtained from the i.r. spectrum which exhibits ν(C≡N) at 2 040 cm^{-1} and ν(C–S) at 808 cm^{-1}; *N*-bonded thiocyanato-complexes generally exhibit ν(C≡N) at or below 2 100 cm^{-1} and ν(C–S) in the 760—880 cm^{-1} region.[12]

While a chelated structure for the above complexes of the diarsine (3) has been assumed, it is recognised that in the solid state a polymeric structure in which the diarsine acts as a bridging ligand is possible and is not ruled out by the above evidence. Indeed, the insolubility of the thiocyanato-complex (see below), its enhanced magnetic moment, and the differences in its crystal-field spectrum compared with those of the halogeno-complexes are not inconsistent with a polymeric structure for this complex, in which there is a greater degree of tetragonal distortion than in the halogeno-complexes.[13] It is hoped to carry out *X*-ray studies of members of the above series in order to resolve these points.

Evidence from molecular-weight determinations, molar conductance, and electronic spectra (Table 2) indicates that the octahedral structure is not retained in solution, dissociation to five-co-ordinate species occurring to a greater or lesser extent depending on the nature of the halogen. (The thiocyanato-derivative was too insoluble for solution studies.) Determination of molecular weights by ebulliometry in chloroform indicates that the extent of dissociation increases from the chloride to the bromide to the iodide, being relatively small in the case of the chloride. This general picture is supported by the molar conductances of the complexes dissolved in nitromethane. The bromo- and iodo-complexes dissociate completely to form 1 : 1 electrolytes,[14] presumably of the type [NiX(dmab)$_2$]X (X = Br or I) containing five-co-ordinate nickel. In the case of the chloro-complex, dissociation is only partial. The electronic spectra of the complexes in nitromethane solution are quite different to the solid-state spectra, exhibiting a strong band in the visible region at *ca.* 15 500 cm^{-1} which moves to lower wavenumber from the chloride to the iodide and increases in intensity. In the case of the chloro- and bromo-complexes, an additional band is observed at *ca.* 20 000 cm^{-1}, which decreases in intensity from the chloride to bromide. In the spectrum of the chloro-complex in nitromethane solution (in which the complex is only partially dissociated according to the conductance data) there is no sign of the band at 9 600 cm^{-1} (ν_1) present in the solid-state spectrum of the octahedral complex. Of the other spin-allowed bands, ν_3 for the octahedral complex coincides with the main absorption band observed in this region for the five-co-ordinate species (see below); similarly ν_4 is obscured

TABLE 2

Complexes of 2,2′-bis(dimethylarsino)biphenyl (dmab) with nickel(II) halides: solution data

Complex	M ^{a}	Λ ^{b} S cm^2 mol^{-1}	Electronic spectra ($\tilde{\nu}_{max.}$/cm^{-1}) ^{c} in	
			MeNO$_2$	CH$_2$Cl$_2$
[NiCl$_2$(dmab)$_2$]	790	45.2	20 150 (840)	18 500 (246)
	(853)		16 000 (610)	9 500 (34)
[NiBr$_2$(dmab)$_2$]	462	80.2	20 900 (700)	16 650 (204)
	(942)		15 900 (1 160)	9 500 (29)
[NiI$_2$(dmab)$_2$]	400	82.9	15 400 (1 420)	15 300 (555)
	(1 036)			

^{a} By ebulliometry in chloroform; calculated values are given in parentheses. ^{b} For 10^{-3} mol dm^{-3} solutions in nitromethane at 25 °C. ^{c} Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

---

[12] R. A. Bailey, S. L. Kozack, T. W. Michelson, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

[13] A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 763.

[14] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

by the intense c.t. band observed above 25 000 cm^{-1} for the five-co-ordinate species. However, a band at *ca.* 9 500 cm^{-1} is observed in the spectra of both the chloro- and bromo-complexes in methylene chloride solution. It is of interest that the main absorption bands in the solution spectra of the chloro- and bromo-complexes in CH_2Cl_2 are at markedly different positions than in nitromethane solution, whereas for the iodo-complex the band positions are similar.

These solution spectra are markedly different to those reported for the corresponding five-co-ordinate complexes of *o*-phenylenebis(dimethylarsine) of the type [NiX(pdma)$_2$]X (X = halide) which exhibit a main broad absorption band at *ca.* 21 000 cm^{-1}, and for which square-pyramidal geometry has been assigned.[15,16] On the basis of the spectroscopic criteria established for differentiating between square-pyramidal and trigonal-bipyramidal nickel(II) complexes, it seems reasonable to infer than in solution in nitromethane the above complexes of the diarsine (3) have a trigonal-bipyramidal structure, since complexes of the latter type exhibit broad absorption bands at *ca.* 15 000 cm^{-1} with a weaker band at *ca.* 20 000 cm^{-1}.[16] The situation in methylene chloride solution is less clear.

Support for the above suggestion of the formation of trigonal-bipyramidal five-co-ordinate species in solution comes from a consideration of the properties of a second series of complexes formed from the diarsine (3) of the type [NiX(dmab)$_2$][ClO$_4$] (X = Cl, Br, or I). This series was prepared by the addition of (3) (2 mol) in hot ethanol to a solution of nickel(II) perchlorate (0.5 mol) and the appropriate nickel(II) halide (0.5 mol) also in ethanol. On cooling the solutions, intensely coloured (blue-green) crystals of the complexes separated. All are diamagnetic, and conductance data in nitromethane solution show that all are 1 : 1 electrolytes, consistent with low-spin five-co-ordinate structures. The electronic spectra of the complexes (Table 3) both in the solid state and in solution in nitromethane are similar, and closely resemble the solution spectra observed for the above [NiX$_2$(dmab)$_2$] complexes. Again it is of interest that in the solution spectra of the halogeno-complex perchlorates the intensity of the band at *ca.* 15 000 cm^{-1} increases from the chloride to iodide, while that of the band at *ca.* 21 000 cm^{-1} decreases and is not observed in the iodo-complex. Attempts to gain further information on the structure of these five-co-ordinate complexes in solution by ^{1}H n.m.r. spectroscopy were frustrated by their low solubility in common n.m.r. solvents.

TABLE 3

Five-co-ordinate (diamagnetic) complexes of 2,2′-bis(dimethylarsino)biphenyl (dmab)

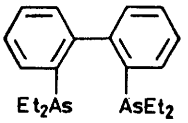
Complex	Colour	Electronic spectra ($\tilde{\nu}_{max.}$/cm^{-1})[a] Solid state	Nitromethane solution	Λ[b] / S cm^2 mol^{-1}
[NiCl(dmab)$_2$]-[ClO$_4$]	Dark blue	14 880	20 400 (750) 15 900 (890)	87.2
[NiBr(dmab)$_2$]-[ClO$_4$]	Dark blue	14 770	21 100 (720), 15 850 (1 140)	86.0
[NiI(dmab)$_2$]-[ClO$_4$]	Dark green	14 570	15 350 (1 440)	86.0

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] For 10^{-3} mol dm^{-3} solutions in nitromethane at 25 °C.

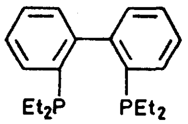
Addition of the diarsine (3) (2 mol) in hot ethanol to a solution of nickel(II) perchlorate (1 mol) also in ethanol gave, on cooling, purple crystals of a complex [Ni(ClO$_4$)$_2$-(dmab)$_2$]. This complex is diamagnetic, and in solution in nitromethane behaves as a 1 : 2 electrolyte, consistent with a four-co-ordinate structure of the type [Ni(dmab)$_2$]-[ClO$_4$]$_2$. Both the solid-state and solution (in nitromethane) electronic spectra are consistent with a square-planar geometry, exhibiting a single absorption at *ca.* 18 000 cm^{-1} (ε 820 dm^3 mol^{-1} cm^{-1}). Addition of one molar proportion of potassium iodide to a solution of the perchlorate complex in nitromethane caused a marked change in colour, and the resulting absorption spectrum is identical with that of the above five-co-ordinate complex [NiI(dmab)$_2$][ClO$_4$], indicating that addition of the iodide ion as fifth ligand occurs very readily. Similar behaviour has been observed for the corresponding four-co-ordinate perchlorate complexes of the diarsines (1) [15] and (2).[2]

The ^{1}H n.m.r. spectrum of the complex [Ni(dmab)$_2$]-[ClO$_4$]$_2$ in solution in trifluoroacetic acid is of interest in that it indicates the inherent dissymmetry of the seven-membered chelate-ring system formed by the diarsine and the metal. Due to the non-planarity of the 2,2′-bridged biphenyl unit, the two methyl groups attached to each arsenic are magnetically non-equivalent and appear as two sharp singlets at τ 8.0 and 8.9. Models indicate that, for each AsMe$_2$ unit, one of the methyl groups is in the plane of the benzene ring to which the arsenic is attached, and is therefore subject to deshielding, whereas the other is sited above the second ring and is therefore shielded. The chelate-ring system is clearly configurationally stable, since rapid inversion about the central biphenyl unit would lead to the two methyl groups on each arsenic becoming magnetically equivalent and a single line spectrum would result.

The diarsine (3) is therefore of considerable interest as a chelating ligand in view of the variety of complexes formed with Ni^{II}. It is of interest to note that the diarsine (4) *fails to complex* with Ni^{II} under a wide range of conditions, in contrast to the corresponding diphosphine (5),[17] which forms only four-co-ordinate



(4)



(5)

---

[15] G. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.

[16] J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, 1970, **92**, 7306.

[17] D. W. Allen, I. T. Millar, F. G. Mann, R. M. Canadine, and J. Walker, *J. Chem. Soc. (A)*, 1969, 1097.

nickel(II) complexes, suggesting that steric considerations in this series must be very critical.

EXPERIMENTAL

Operations involving 2,2′-bis(dimethylarsino)biphenyl (3, dmab), which was prepared as described in the literature,[4] were conducted under nitrogen. Magnetic susceptibilities of complexes were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant and are corrected for diamagnetic effects. Diffuse-reflectance and solution spectra were recorded using a Pye–Unicam SP 700 spectrophotometer. The diffuse-reflectance spectra were obtained using magnesium oxide as the reference (and diluant as necessary). Molar conductivities were determined at a concentration of 10^{-3} mol dm^{-3} in nitromethane solution at 25 °C using a Wayne–Kerr bridge. Molecular weights were determined ebulliometrically in solution in chloroform.

Pseudo-octahedral Complexes of (3) *with Nickel*(II) *Halides and Thiocyanate*.—*General procedure*. To a solution of the diarsine (2 mol) dissolved in hot ethanol was added a solution of the nickel(II) halide or thiocyanate (1 mol), also in ethanol. On cooling, the complexes crystallised, and after filtration were washed with ethanol and dried. The complexes prepared were as follows. *Bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*dichloronickel*(II), green crystals (Found: C, 45.05; H, 5.0. $C_{32}H_{40}As_4Cl_2Ni$ requires C, 45.0; H, 4.7%); *bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*dibromonickel*(II), green crystals (Found: C, 41.2; H, 4.05. $C_{32}H_{40}As_4Br_2Ni$ requires C, 40.75; H, 4.30%); bis[2,2′-bis(dimethylarsino)-biphenyl]di-iodonickel(II), olive-green crystals. A satisfactory analysis could not be obtained for the last complex even after recrystallisation and prolonged drying. The carbon figures were consistently high, possibly due to trace amounts of occluded arsine (Found: C, 39.7; H, 4.15. $C_{32}H_{40}As_4I_2Ni$ requires C, 37.05; H, 3.9%). However, in view of the similarity of its properties (Tables 1 and 2) to those of the other halogeno-complexes, there seems to be little doubt about its constitution. *Bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*di-isothiocyanatonickel*(II), grey-green crystals (Found: C, 45.2; H, 4.3; N, 3.2. $C_{34}H_{40}As_4N_2NiS_2$ requires C, 45.4; H, 4.5; N, 3.1%), $\bar{\nu}$ (KBr) 2 040s [$\nu(C\equiv N)$] and 808w cm^{-1} [$\nu(C-S)$].

Five-co-ordinate Halogeno-complex Perchlorates (3).—*General procedure*. To a solution of the diarsine (2 mol) in hot ethanol was added a solution of hydrated nickel(II) perchlorate (0.5 mol) and the appropriate nickel(II) halide (0.5 mol) also in ethanol. On cooling, crystals of the respective complexes formed, and after filtration were washed with ethanol and dried. The complexes formed were: *bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*chloronickel*(II) *perchlorate*, deep blue crystals (Found: C, 42.05; H, 4.4. $C_{32}H_{40}As_4Cl_2NiO_4$ requires C, 41.85; H, 4.4%); *bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*bromonickel*(II) *perchlorate*, deep blue crystals (Found: C, 40.05; H, 4.15. $C_{32}H_{40}As_4BrClNiO_4$ requires C, 39.9; H, 4.20%); and *bis*[2,2′-*bis*(*dimethylarsino*)*biphenyl*]*iodonickel*(II) *perchlorate*, dark green crystals (Found: C, 38.25; H, 4.15. $C_{32}H_{40}As_4ClINiO_4$ requires C, 38.05; H, 4.0%).

Square-planar Complex with Nickel(II) *Perchlorate*.—To a solution of the diarsine (2 mol) in hot ethanol was added a solution of nickel(II) perchlorate (1 mol) also in ethanol. On cooling, purple crystals of the complex separated and after filtration were washed with ethanol and dried (Found: C, 39.05; H, 4.2. $C_{32}H_{40}As_4Cl_2NiO_8$ requires C, 39.15; H, 4.1%), diamagnetic, Λ ($MeNO_2$, 10^{-3} mol dm^{-3}) 168 S cm^2 mol^{-1}, $\bar{\nu}_{max.}$ (solid state) 18 182 cm^{-1}, ($MeNO_2$ solution) 17 889 cm^{-1} (ε 820 dm^3 mol^{-1} cm^{-1}). Addition of potassium iodide (1 mol) to a solution of the complex in nitromethane caused an abrupt colour change, and the solution spectrum exhibited a single broad absorption band at 15 337 cm^{-1}.

[6/2094 *Received*, 15*th November*, 1976]