Co-ordination Complexes Containing Multidentate Ligands. Part II.[1] Five-co-ordinate Nickel(II) and Cobalt(II) Complexes Containing Tridentate Ligands with Group VB Donors

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The ligands L, bis(o-diphenylarsinophenyl)phenylarsine (ptas) and bis(o-diphenylarsinophenyl)phenylphosphine (pdap) form low-spin five-co-ordinate complexes of formulae $[Ni_2L_3(H_2O)](ClO_4)_4$, $[NiLX_2]$ (X = Br or I), and $[CoLX_2]$ (X = Br or NCS). I.r. and visible spectra have been used in assigning square-pyramidal structures to the complexes. The complexing ability of these ligands is compared with that of similar ligands with aliphatic substituents on the arsenic atoms.

THERE are few reports of complexes of tridentate ligands containing heavy donor atoms.[2] The triarsine, bis(3-dimethylarsinopropyl)methylarsine (tas), forms low-spin five-co-ordinate $[Ni(tas)X_2]$ (X = Br or I)[3] and the

five-co-ordinate dimer $[Ni_2(tas)_3(H_2O)](ClO_4)_4$.[4] The analogous bis(3-dimethylarsinopropyl)phenylphosphine (dap) forms similar complexes.[4,5] Both the tas and dap complexes are quite stable to oxidation in air and dissociation in solution, and the complexing ability of these ligands to first-row transition metal ions must be due, in

[1] Part I, L. Baracco and C. A. McAuliffe, *J.C.S. Dalton,* 1972, 948.

[2] M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.,* 1967, **6**, 1543.

[3] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.,* 1961, 4433.

[4] C. A. McAuliffe, M. O. Workman, and D. W. Meek, *Inorg. Nuclear Chem.,* 1969, **5**, 147.

[5] C. A. McAuliffe, D. W. Meek, and M. O. Workman, *J. Co-ordination Chem.,* in the press.

part, to the increased σ-donor ability of arsenic atoms with aliphatic substituents. In fact, apart from the mainly aliphatic diarsine, o-phenylenebisdimethylarsine,[6] and the quadridentate tris(o-diphenylarsinophenyl)-arsine[7] and tris(o-dimethylarsinophenyl)arsine,[8] there are very few arsenic ligands which complex with nickel(II) and cobalt(II); the only examples of isolable mono-dentate arsine complexes are [Ni(AsEt₃)₂I₂][9] and [Ni{AsMe₂(p-MeNHC₆H₄)}X₂] (X = Br or I).[10]

We have studied the complexing properties of two tridentate ligands, bis(o-diphenylarsinophenyl)phenyl-arsine (ptas) and bis(o-diphenylarsinophenyl)phenyl-phosphine (pdap), towards nickel(II) and cobalt(II) salts. The major points of interest were the general stability of the complexes formed by these aromatic ligands and the stoicheiometry of the complexes formed with Ni(H₂O)₆(ClO₄)₂.

EXPERIMENTAL

Metal salts were obtained from B.D.H. Ltd., and the ligands were prepared as previously reported.[11]

RESULTS AND DISCUSSION

The complexes isolated, together with analytical and other data, are listed in Table 1. A great deal of difficulty was experienced in isolating the complexes in a pure state. No reaction of the metal salts and the ligands was found to take place in ethanol, and reaction in n-butanol was never complete, some ligand always precipitating with the complexes. Although a reaction medium such as dichloromethane is not normally used for synthesizing metal complexes of the type discussed here, mainly because of its volatility and also its great ability to dissolve the resulting complexes, we found that it was the only medium from which pure solid complexes could be isolated. From our observations of colour changes upon mixing reactants and ease of isolation of the resulting complexes, which we propose gives a broad indication of the stability of the complexes, it was clear that pdap had more affinity for complexation than did ptas, presumably because of the increasing σ-donor ability of the phosphorous atom in pdap. Similarly, nickel formed more complexes than did

TABLE 1

Analytical data and physical properties of the complexes

Complex	Colour	$10^6\chi_M$ a	Analyses: % Found (% Calc.)		
			C	H	Halogen
[Ni(pdap)Br₂]	Deep blue	214	53·6 (53·8)	3·7 (3·5)	16·8 (17·1)
[Ni(pdap)I₂] b	Black	187	49·2 (48·9)	3·2 (3·2)	24·4 (24·7)
[Ni₂(pdap)₃(H₂O)](ClO₄)₄	Black	94	56·8 (56·3)	3·9 (3·8)	
[Ni(ptas)Br₂]	Deep blue	190	51·2 (51·4)	3·6 (3·4)	16·7 (16·3)
[Ni(ptas)I₂]	Black	253	46·2 (46·9)	2·9 (3·1)	23·8 (23·6)
[Ni₂(ptas)₃(H₂O)](ClO₄)₄	Black	104	53·9 (53·6)	3·6 (3·6)	
[Co(pdap)Br₂]	Deep green	2·23 c	53·9 (53·8)	3·7 (3·5)	16·8 (17·1)
[Co(pdap)(NCS)₂] d	Deep green	2·30 c	58·2 (59·1)	3·4 (3·7)	3·4 (3·1) e

a χ_M is the corrected molar susceptibility in c.g.s. units. All of the nickel complexes are effectively diamagnetic with paramagnetic contribution from the temperature-independent paramagnetism. b Molar conductance value, Λ_M, was found to be 6 Ω^{-1} cm² mol⁻¹ in 10⁻³M solution in MeNO₂ (a typical value for a 1 : 1 electrolyte in this solvent is 80—100 Ω^{-1} cm² mol⁻¹). c μ_{eff}. Values. d This complex exhibits no measurable conductance in dichloromethane. e Nitrogen analysis.

The complexes were prepared by the following general method. The appropriate quantity of metal salt, dissolved in the minimum quantity of ethanol, was added dropwise to a stirred solution of the ligand (1·0 g) in the dichloro-methane (50 ml), metal : ligand ratio 1·1 : 1 for halides and thiocyanates, 2·1 : 3 for perchlorate). After stirring the deeply coloured solutions for 15 min, slow addition of diethyl ether (150 ml) led to precipitation. The solid complexes were filtered, redissolved in dichloromethane, refiltered to remove any unreacted metal salts, and re-precipitated with ether.

Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. I.r. spectra were measured in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckman DK2 spectrophotometer (for reflectance spectra BaSO₄ was used as a diluant). Magnetic measurements were carried out by the Gouy method.

cobalt, and this may well reflect the supposedly slightly ' softer ' character of nickel as an acceptor atom. Of the metal halides used it was clear that the order I > Br ≫ Cl reflects the acceptor properties of the metal halides towards ptas and pdap. It must be emphasized that no measurements of the stability of the complexes were carried out. However, there has recently been some discussion of the importance of π-bonding, particularly in complexes containing the Group Vʙ donors,[12] and we believe that our observations of the tendency of different metal halides to react with ptas and pdap may prove to be of interest to those involved in discussions of bonding in Group Vʙ complexes.

The only complexes which could be isolated in the reaction with hydrated nickel perchlorate were the

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

[7] G. Dyer, G. J. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.

[8] O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, 4, 93.

[9] K. A. Jensen, *Z. anorg. Chem.*, 1936, 229, 265.

[10] R. C. Cass, G. E. Coates, and R. G. Hayter, *J. Chem. Soc.*, 1955, 4007.

[11] T. E. W. Howell, S. A. Pratt, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 3167.

[12] L. M. Venanzi, *Chem. in Britain*, 1968, 162; R. J. P. Williams, *ibid.*, 1968, 277.

dimeric [Ni$_2$L$_3$(H$_2$O)](ClO$_4$)$_4$ (L = ptas or pdap). No simple 1 : 1 or 1 : 2 nickel perchlorate–ligand complexes appear to be isolable. Analytical data fit only this dimeric formulation. I.r. spectra show the presence of

TABLE 2

Electronic absorption spectra of the complexes

Complex	Solution ^{a} (cm^{-1})	Solid
[Ni(pdap)Br$_2$]	14,710 (200) ^{b}	
	20,510 (2070)	20,530
	33,900 (4760)	34,150
[Ni(pdap)I$_2$]	13,600 (130)	
	19,990 (1330)	19,970
	27,780 (10,870)	27,900
	34,010 (20,790)	34,300
[Ni$_2$(pdap)$_3$(H$_2$O)](ClO$_4$)$_4$	16,350sh	16,500sh
	18,605 (7090)	18,700
	26,650 (41,700)	26,920
	34,190 (51,800)	34,200
[Ni(ptas)Br$_2$]	14,500sh	
	19,195 (1990)	19,220
	33,450sh	34,050
[Ni$_2$(ptas)I$_2$]	12,900 (77)	12,800
	17,910 (1630)	17,980
	26,100sh	27,030
[Ni$_2$(ptas)$_3$(H$_2$O)](ClO$_4$)$_4$	15,500sh	15,800sh
	17,910 (6390)	18,010
	21,830 (3740)	21,870
	25,970 (34,610)	26,100
	38,240sh	37,970
[Co(pdap)Br$_2$]	5700 (39)	
	5990 (38)	5950
	6260	
	14,290 (364)	14,330
	17,240 (675)	17,330
	23,530sh	23,700
	34,100sh	34,210

^{a} In dichloromethane. Extinction coefficients in parentheses.
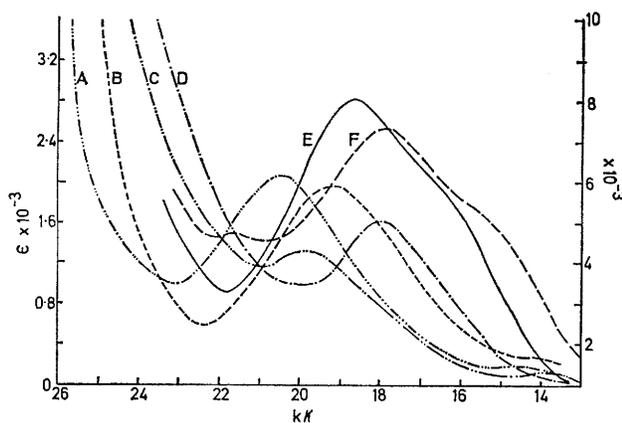
FIGURE 1 Visible spectra of the nickel(II) complexes; A, Ni(pdap)Br$_2$; B, Ni(ptas)Br$_2$; C, Ni(pdap)I$_2$; D, Ni(ptas)I$_2$; E, [Ni$_2$(pdap)$_3$(H$_2$O)](ClO$_4$)$_4$; F, [Ni$_2$(ptas)$_3$(H$_2$O)](ClO$_4$)$_4$

water vibrations at ca. 3300 and 1650 cm^{-1}.[13] The solid state and solution electronic spectra of these diamagnetic complexes (Table 2, Figure 1) are quite similar and indicate the same geometry in both physical states.

[13] S. F. Pavkoic and D. W. Meek, Inorg. Chem., 1965, 4, 1091.

[14] A referee has pointed out that absorptions with ε = 6000—7000 are extremely high. Venanzi has reviewed his work on complexes similar to those reported here (M. J. Norgett, T. H. M. Thornley, and L. M. Venanzi, Co-ordination Chem. Rev., 1967, 2, 99), and has shown that these visible bands, with ε up to 8000, are essentially d–d transitions.

The presence of an intense absorption at ca. 18 kK with a pronounced shoulder at lower energy is indicative of a square-pyramidal geometry and the structure is probably very similar to that of the [Ni$_2$L$_3$(H$_2$O)]$^{4+}$ (L = tas or dap) dimers. Molecular models indicate that the flexible tas and dap ligands can quite readily adopt the necessary conformations to fit the proposed structure,[4] but the more rigid ptas and pdap ligands do not easily adopt this configuration. Nevertheless, electronic
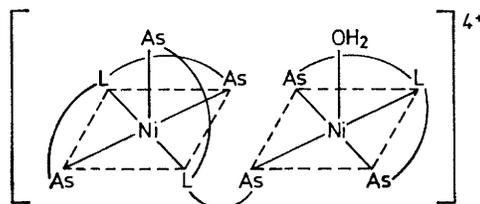
spectra strongly suggest similar structures for both sets of complexes. Because there are two different cations in the proposed dimer it is not surprising that the main electronic absorption band is so asymmetrical. As expected, the ptas and pdap complexes absorb at lower energies than do their aliphatic analogues. A more striking difference is observed in the extinction co-efficients of the main visible absorption band. For this band, in the tas and dap dimers ε = 800—1000, but in the ptas and pdap dimers ε = 6000—7000. The phenomenon of increased extinction coefficient of absorption bands of nickel(II) arsine complexes with aromatic instead of aliphatic substituents has been investigated.[8] It was postulated that ligand field bands can 'borrow' intensity from π* ◄— π transitions of the phenyl groups attached to the arsenic atoms.[14]

There have been several reports recently of the reduction of perchlorate ion to chloride by tertiary phosphines.[4,15,16] All attempts to bring about reduction of the perchlorate groups in [Ni$_2$(pdap)$_3$(H$_2$O)]-(ClO$_4$)$_4$ resulted in almost immediate decomposition of the complex.

The tridentate ligands react with nickel bromide and iodide to form the complexes [NiLX$_2$] (L = ptas or pdap; X = Br or I). The complexes are diamagnetic and are easily decomposed by dissolution in such solvents as alcohols, nitromethane, acetonitrile, and nitrobenzene. Thus, conductance data could not be obtained except for the [Ni(pdap)I$_2$] complex, which was sufficiently stable in nitromethane for a conductivity measurement at ca. 10^{-3}M concentration. It is essentially a non-electrolyte (Table 1).

The energies and general contours of the electronic absorption spectra of the NiLX$_2$ complexes are similar to those of the [Ni(tas)X$_2$][3] and [Ni(dsp)I$_2$] [dsp = bis(o-methylthiophenyl)phenylphosphine] [2] complexes. Since both [Ni(tas)Br$_2$] [17] and [Ni(dsp)I$_2$] [18] have been

[15] E. W. Abel and S. P. Tyfield, Chem. Comm., 1969, 465.

[16] L. V. Interrante and G. V. Nelson, Inorg. Chem., 1968, 7, 1059.

[17] G. A. Mair, H. M. Powell, and D. E. Henn, Proc. Chem. Soc., 1962, 415.

[18] D. W. Meek, and J. A. Ibers, Inorg. Chem., 1969, 8, 1915.

shown by X-ray studies to be discrete five-co-ordinate molecules with approximately square-pyramidal geometry, it seems highly probable that the complexes studied here have a similar structure, viz:

(L = P or As)
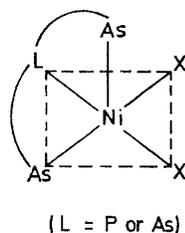
As can be seen from Table 2 and Figure 1, the pdap complexes absorb at higher energy than the ptas complexes, as expected from the normal spectrochemical series, P > As.[19,20] A change of halides also produces the normal Br > I spectrochemical shift. The main ligand field band, which occurs at 17—19 kK, can be assigned to the transition of d-orbital character $d_{z^2} \longrightarrow d_{x^2-y^2}$.[21] In many of the spectra (Table 2) there also occurs a very intense band $ca.$ 34 kK. Although the energy of this absorption seems rather high for a ligand–metal electronic transition, the fact that it appears in the perchlorate complexes rules out the possibility of it being due to halogen–metal charge transfer. Thus, we tentatively assign this band to the arsenic–nickel electronic transition involving the lone pair of electrons of arsenic and the empty $b_1(d_{x^2-y^2})$ orbital of nickel.

When solutions of ptas and cobalt(II) salts were mixed, the only colour change observed was with CoI_2, but no complex could be isolated. The pdap ligand produced green colours with many Co^{II} salts, but the only pure complexes we isolated were the bromo- and isothiocyanato-derivatives.

Several studies of low-spin five-co-ordinate Co^{II} complexes have been made: Horrocks [22] studied the $[Co(diphos)_2X]^+$ complexes, Meek [23] prepared a series of $[Co(bidentate)_2X]^+$ compounds, and Venanzi [24] has prepared the $[Co(qp)X]^+$ [qp = tris(o-diphenylphosphinophenyl)phosphine] series. The electronic spectra of these five-co-ordinate complexes have rather similar features, which seems to be independent of the proposed square-pyramidal [22,23] or trigonal-bipyramidal [24] geometry; namely, bands in the 6—9, 14—17, and 19—25 kK regions. The two complexes prepared by us have similar spectra (Table 2, Figure 2) and, hence, presumably have similar structures. Some information helpful in assigning a structure may be gained from the i.r. spectrum of the $[Co(pdap)(NCS)_2]$ complex. In the $\nu(C{\equiv}N)$ region a single absorption at 2074 cm^{-1}, characteristic of N-bonded thiocyanate is observed. The fact

that no absorption appears at $ca.$ 2050 cm^{-1} rules out the possibility of ionic thiocyanate (and, thus, a four-co-ordinate Co^{II} complex), and this complex is also a non-electrolyte in dichloromethane. Moreover, the single absorption indicates similar NCS environments, and, thus, the square-pyramidal structure assigned to the $[NiLX_2]$ complexes may tentatively be assigned to the $[Co(pdap)(NCS)_2]$ complex. Of course, a structure involving a trigonal-bipyramidal complex with $trans$-NCS groups is also a possibility, but a square-pyramidal configuration involving NCS groups in both axial and equatorial positions may be ruled out as this would most likely lead to a split $\nu(C{\equiv}N)$ band. However, because of the added complication of Jahn–Teller effects, and in the absence of X-ray structural data, we have thus made no attempt to assign any of the observed d–d bands in the electronic spectra. Because of the similarity of the visible spectra in the solid state and in dichloromethane solution the complexes presumably have the same structure in both physical states. The magnetic moments of the Co^{II} complexes are 2·23 B.M.
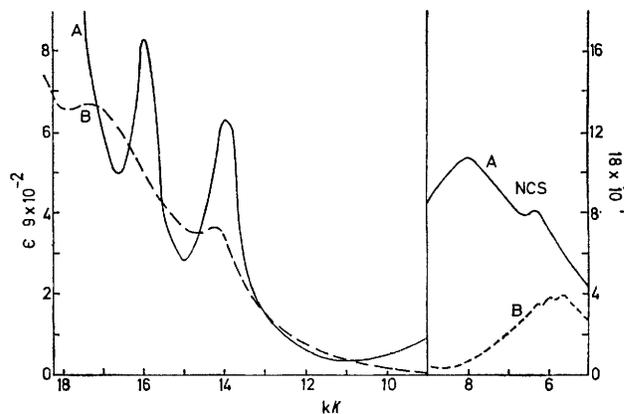
FIGURE 2 Visible spectra of the cobalt(II) complexes; A, [Co(pdap)(NCS)₂]; B, [Co(pdap)Br₂]

(Br$^-$) and 2·30 B.M. (NCS$^-$) and may be compared with a range of 1·8—2·0 B.M. for low-spin octahedral Co^{II} complexes and 2·3—2·9 B.M. for low-spin planar Co^{II} complexes.[25]

Cunninghame et $al.$,[26] have prepared the low-spin complexes $[Co(ttas)_2][CoCl_4]$ and $[Co(ttas)_2](ClO_4)_2$ [ttas = bis(o-dimethylarsinophenyl)methylarsine] which contain the octahedral $[Co(ttas)_2]^{2+}$ cation. These workers stated that they were unable to prepare any five-co-ordinate complexes. A comparison of the C.F.S.E. for low-spin octahedral (-18 Dq) and low-spin square-pyramidal (-10 Dq) Co^{II} complexes [27] shows that the former has a higher C.F.S.E. than the latter

[19] J. Chatt, G. A. Gamlen, and L. E. Orgel, $J.$ $Chem.$ $Soc.$, 1959, 1047.

[20] A. Pidcock, R. E. Richards, and L. M. Venanzi, $J.$ $Chem.$ $Soc.$ (A), 1968, 1970.

[21] C. A. McAuliffe and D. W. Meek, $Inorg.$ $Chem.$, 1969, 8, 904.

[22] W. DeW. Horrocks, jun., G. R. Van Hecke, and D. DeW. Hall, $Inorg.$ $Chem.$, 1967, 6, 694.

[23] G. Dyer and D. W. Meek, $J.$ $Amer.$ $Chem.$ $Soc.$, 1967, 89, 3983.

[24] J. G. Hartley, D. G. E. Kerfoot, and L. M. Venanzi, $Inorg.$ $Chim.$ $Acta$, 1967, 1, 145.

[25] B. N. Figgis and R. S. Nyholm, $J.$ $Chem.$ $Soc.$, 1954, 12.

[26] R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, $J.$ $Chem.$ $Soc.$, 1964, 5800.

[27] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1963, p. 57.

configuration. Since ligand field strength of ttas is expected to be much greater than that of ptas or pdap, this difference in C.F.S.E. for six- vs. five-co-ordination is more pronounced for ttas complexes. Moreover, the bulkiness of the o-phenyl substituents on the terminal arsine donors in ptas and pdap make the formation of $[CoL_2]^{+2}$ complexes with these ligands very sterically crowded and thus very unstable. It is probably for these reasons that $[Co(ttas)_2]^{+2}$ and $[Co(pdap)X_2]$ complexes are obtained for these ligands.

CONCLUSION

These tridentate ligands, while providing some rare examples of $-AsPh_2$ co-ordination to Ni^{II} and Co^{II} ions appear, nevertheless, to be poor donors to these ions. It is also clear that this type of tridentate ligand prefers to effect five-co-ordination about the metal ions used in this study, even when this involves the sterically encumbered $[Ni_2L_3(H_2O)]^{4+}$ cation.