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Bidentate Group VB Ligands.
Part XIII. Divalent Cobalt, Nickel, and Palladium Complexes of 1,2-Bis(methylphenylarsino)ethane and 1,3-Bis(methylphenylarsino)propane. Stoichiometric and Structural Effects of Chelate Chain Length

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Thirtyfour complexes of 1,2-bis(methylphenylarsino)ethane (dase) and 1,3-bis(methylphenylarsino)propane (dasp) have been characterised. Interesting differences are observed in the complexing properties of these chelates. Thus, with cobalt(II) halides $[Co(dase)_2][CoX_4]$*, which contain planar cations, and pseudotetrahedral* $[Co(dasp)X_2]$ *are obtained. Nickel (II) halides form planar* $[NiLX_2]$ *complexes with dase, but with dasp form* $[Ni(dasp)X_2]_n$ *(X = Cl, Br) which are pseudooctahedral in the solid state and planar in solution, and the pseudotetrahedral* $[Ni(dasp)I_2]$*. The* $[Ni(dasp)_2X]ClO_4$ *are trigonal bipyramidal in the solid state (X = Cl, Br, I, NCS), but in solution* $[Ni(dasp)_2(NCS)]^+$ *appears to be square pyramidal, whilst the* $[Ni(dase)_2X]ClO_4$ *are square pyramidal in both the solid state and solution. The planar* $[Ni(dasp)(NCS)_2]$ *complex differs from the analogous dase species by losing ligand on recrystallisation to form the dimeric* $Ni_2(dasp)_3(NCS)_4$ *moiety. Planar* $[PdLX_2]$ *(L = dase, dasp, X = Cl, Br, I) species are formed, but no* $[PdL_2X]^+$ *complexes could be isolated. In the solid state* $[PdL(NCS)(SCN)]$ *complexes are formed, and the dase species isomerises to* $[Pd(dase)(SCN)_2]$ *in dichloromethane. An attempt is made to relate the structural differences in the complexes to the chain length of the chelates.*

Introduction

The vast majority of bidentate group VB donor ligands whose coordination chemistry has been studied [2, 3] have contained C_2 chelate linkages – dimethylene, vinyl, or *o*-phenylene. Where studies have been extended to ligands with longer backbones interesting differences in the type of complex formed have been observed. Thus, diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ produce planar $NiLX_2$ (X = halide) and pentacoordinate square pyramidal $[NiL_2X]^+$ complexes (n = 1,2), and also tetrahedral $NiLX_2$ (n = 4,5) [2]. The intermediate case (n = 3) forms $NiLX_2$ complexes which are planar in the solid state, but exhibit planar $\rightleftharpoons$ tetrahedral isomerism in solution [4]. However, the analogous alkylsubstituted diphosphine, 1,3-bisdimethylphosphinopropane (dmp) [5] forms $NiLX_2$ complexes which are planar both in the solid state and in solution; this may be due to the smaller size of the substituents on the phosphorus or, more likely, the increase in σ-donor power. The pentacoordinate $[Ni(dmp)_2X]^+$ ions are interesting in that for X = Br, I the structures are trigonal bipyramidal, whilst for X = Cl, NCS the intermediate geometry of C_s microsymmetry is observed.

We report here our studies on cobalt(II), nickel(II), and palladium(II) complexes with two ditertiary arsines, 1,2-bis(methylphenylarsino)ethane (dase) and 1,3-bis(methylphenylarsino)propane (dasp).* With these ligands we can observe the effects of changes in chelate chain length, ligands with both phenyl and methyl substituents, and arsenic instead of phosphorus donors.

Experimental

1,2-Bis(methylphenylarsino)ethane was prepared as described by Bosnich and Wild [6] and characterised as the dimethiodide (Found: C, 33.7; H, 4.6; I, 39.5. $C_{18}H_{26}As_2I_2$ requires C, 33.5; H, 4.0; I, 39.3%).

1,3-Bis(phenylmethylarsino)propane was obtained similarly from 1,3-bis(phenylchloroarsino)propane [7] and 2MeMgI. The product (yield 65% based on the chloroarsine) was an air-sensitive oil, b.pt. 168–172 °C/0.05 torr, which readily formed the dimethiodide (Found: C, 34.5; H, 4.6; I, 38.2. $C_{19}H_{28}As_2I_2$ requires C, 34.5; H, 4.3; I, 38.3%).

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*For part XII see ref. 1.

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**Meso* and *dl* forms of these ligands exist. The complexes prepared will contain different amounts of these isomers according to the solvent from which they were isolated. We make no attempt to discuss this phenomenon here.

The preparation of dase complexes are described below; those of dasp are similar unless otherwise noted.

[Pd(dase)Cl₂]

A solution of sodium tetrachloropalladate(II) (0.3 g, 1 mmol) in ethanol (20 cm^3) was treated with dase (0.37 g, ~1 mmol) in dichloromethane (10 cm^3). The orange-brown solution was stirred briefly, evaporated to dryness, and recrystallised from ethanol/dichloromethane. Yield ~80%.

[Pd(dase)X₂] (X = Br, I, NCS)

These were prepared similarly in the presence of excess NaX.

$[Ni(dase)_2](ClO_4)_2$

Nickel(II) perchlorate hexahydrate (0.37 g, 1 mmol) and dase (0.72 g, 2 mmol) were refluxed together under nitrogen for 30 min. in n-propanol (30 cm^3). The solution was concentrated to ~8 cm^3 and a yellow precipitate formed. This was filtered and recrystallised from dichloromethane/n-propanol. Yield 95%.

$[Ni(dase)Cl_2]$

Hydrated nickel(II) chloride (0.24 g, 1 mmol) and dase (0.36 g, 1 mmol) were briefly warmed together in a 1:1 mixture of dichloromethane/n-propanol (20 cm^3), the dichloromethane then being removed under a stream of nitrogen. Addition of diethylether (30 cm^3) caused the complex to precipitate. The solid was filtered, dissolved in dichloromethane and reprecipitated by careful addition of diethylether. Yield 65%. *$[Ni(dase)_2]^+$ (X = Br, I, NCS)* were obtained similarly. $[Ni(dase)Cl_2]$ and $[Ni(dasp)X_2]$ (X = Cl, Br, I) were found to decompose slowly on standing in dichloromethane solution, and thus isolation of the solid was done as quickly as possible.

$[Ni(dase)_2X]ClO_4$ (X = Cl, Br, I, NCS)

A solution of equimolar amounts of NiX_2 and $Ni(ClO_4)_2{\cdot}6H_2O$ was obtained in either n-propanol or n-butanol (30 cm^3). The ligand (2 equivalents) was syringed in and the mixture refluxed under nitrogen for 30 min. The solution was concentrated to ~10 cm^3 and allowed to cool. The deeply coloured products which separated were recrystallised from dichloromethane/n-hexane. Yields 70–85%.

$[Ni(dasp)(NCS)_2]$

A solution of $Ni(NCS)_2$ in n-butanol was prepared from KNCS and $Ni(NO_3)_2{\cdot}6H_2O$. Addition of one equivalent of dasp, followed by stirring for 30 min, yielded a brown–yellow solution. Addition of diethylether led to precipitation of the complex. The complex decomposed on attempted recrystallisation yielding a brown solid, $Ni_2(dasp)_3(NCS)_4$ and yellow $Ni(NCS)_2$.

$[Co(dase)X_2]$ (X = Cl, Br, I)

These were prepared in a similar manner to the nickel(II) analogues from the hydrated cobalt(II) halide and the ligand in n-butanol. Unlike the nickel(II) analogues these complexes do not decompose on standing in solution. Yields ~80%.

$[Co(dase)_2](ClO_4)_2$

Cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) and dase (1.53 g, 2.2 mmol) were stirred in an equal mixture of ethanol/dichloromethane (30 cm^3). After ~10 min an orange–red precipitate formed, which was filtered and recrystallised from dichloromethane. Yield 70%.

Physical measurements

These were performed as previously reported [8]. Elemental analyses were performed by the microanalytical service of this Department.

Results and Discussion

The ligands 1,2-bis(methylphenylarsino)ethane (dase) and 1,3-bis(methylphenylarsino)propane (dasp) were produced by reaction of two equivalents of methylmagnesium iodide with the appropriate α, ω-bis(phenylchloroarsino)alkanes [6, 7]. After vacuum distillation colourless air-sensitive oils were obtained which readily afforded crystalline dimethiodides. The ligand ^1H n.m.r. spectra indicate the presence of approximately equal amounts of *meso* and *rac* isomers. The spectrum of dase has been reported previously [6]; that of dasp shows a phenyl multiplet (2.68 τ), methylene multiplet (8.32 τ), and methyl resonances (8.82 τ, 8.87 τ) with integrated intensities $Ph:CH_2:CH_3$ 10:6:5.9 (calculated 10:6:6). Routine ^1H n.m.r. spectra of the metal complexes were recorded where possible, but apart from showing the presence of isomeric forms were generally too complex for analysis due to spreading out of the methylene resonances [6, 9] and, in a few cases, to the coincidence of methyl and methylene signals. The electronic spectra of the isomers of $Pd(dase)Cl_2$ are essentially identical [6], and since the purpose of the present study was to examine the electronic spectral and structural differences in the dase and dasp complexes, separation of the isomers was not attempted.

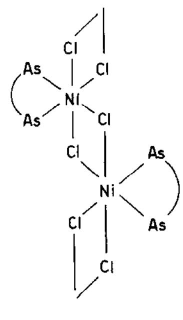
Palladium(II) Complexes

Both ligands afforded planar $PdLX_2$ (X = Cl, Br, I, NCS) complexes, but attempts to isolate $[PdL_2X]^+$ species were unsuccessful even in the presence of a considerable excess of ligand. A comparison of the electronic spectra of the corresponding halide complexes of dase and dasp (Table) shows that the former absorb at higher energy, a reflection of the greater ligand field strength of the five-membered chelates over the six-membered chelates. Attempts to prepare pentacoordinate cations with $Et_2PCH_2CH_2PEt_2$ [10] were also unsuccessful although such species readily form with o-$C_6H_4(AsMe_2)_2$ [11], $Ph_2AsCH_2CH_2AsPh_2$ [12], and o-$C_6H_4(AsPh_2)_2$ [13].

The mode of coordination of thiocyanate ligands in compounds of the type Pd(bidentate)$(CNS)_2$* has attracted much interest recently [14]. In the solid state both [Pd(dase)(NCS)(SCN)] and [Pd(dasp)(NCS)(SCN)] complexes contain both *N*- and *S*-bonded thiocyanate groups as evidenced by their mull infrared spectra which exhibit ν(CN) at 2105, 2080 and 2110, 2070 cm^{-1}, respectively. In dichloromethane solution the structure of [Pd(dasp)(NCS)(SCN)] is unchanged, the absorptions occurring at 2115 cm^{-1}, sharp ($\nu_{1/2}$ = 12 cm^{-1}; A = 2.3 $\times$ 10^4 cm^{-2} M^{-1}) and 2080 cm^{-1}, broad ($\nu_{1/2}$ = 40 cm^{-1}; A = 11.1 $\times$ 10^4 cm^{-2} M^{-1}). However, in dichloromethane [Pd(dase)(NCS)(SCN)] undergoes almost complete isomerisation to the totally S-bonded form $[Pd(dase)(SCN)_2]$; one strong, sharp absorption appears at 2115 cm^{-1} ($\nu_{1/2}$ = 14 cm^{-1}; A = 3.1 $\times$ 10^4 cm^{-2} M^{-1}) and there is only an exceedingly weak band present at 2070 cm^{-1} indicating a very small amount of Pd–NCS linkages. At first sight these results would seem to confirm the recent postulation of Palenik, Meek and co-workers [15] that the mode of palladium(II)–thiocyanate coordination is essentially dependent on steric factors – based on their crystallographic work on $[Pd(Ph_2P(CH_2)_nPPh_2)(CNS)_2]$ systems which show N,S coordination for n = 2 but N,N coordination for n = 3. The explanation of Palenik *et al.* [15] is that the bent –SCN linkage increasingly interacts with the terminal groups on the phosphorus as the $\widehat{P{-}Pd{-}P}$ increases, *i.e.* as the chelate chain length increases. The steric interaction in the cases of $PhMeAs(CH_2)_nAsMePh$ will be less than for the diphosphines and hence N,S coordination is possible for both C_2 and C_3 diarsine systems. However, we remain unconvinced [13, 16] that either electronic factors such as antisymbiosis [17] or steric factors are sufficient by themselves to explain all phenomena observed. Particularly germane to the present study of the $[Pd(dase)(CNS)_2]$ complex (N,S solid→S,S solution) is the observation of the similar C_2 backbone ligand 1,2-bis(diphenylarsino)ethane (dae) forming the complex $[Pd(dae)(CNS)_2]$ (S,S solid→N,S solution) [14]. It is clear that one simple explanation for palladium(II)–thiocyanate coordination is not enough.

Nickel(II) Complexes

The dase ligand reacts with NiX_2 (X = Cl, Br, I, NCS) in a 1:1 ratio to produce $[Ni(dase)X_2]$ species, which on the evidence of their electronic spectra (Table) in solution and in the solid state have a planar configuration. Consistent with this the complexes are diamagnetic and non-electrolytes, and show two ν(Ni–X) absorptions (X = Cl, Br) in their far IR spectra. The chloro complex dissolves in dichloromethane to form a deep purple solution which slowly becomes cloudy, indicating slow decomposition. The IR spectrum of $[Ni(dae)(NCS)_2]$ exhibits one broad band at 2070 cm^{-1} indicating that both anions are N–bonded [14]. The dase complexes are comparable with those of other bidentate group VB ligands with C_2 backbones, *e.g.* $Et_2PCH_2CH_2PEt_2$ [10], *cis*-$Ph_2PCH{=}CHPPh_2$ [18] (vpp), and $Ph_2PCH_2CH_2PPh_2$ [4] (dpe), but differ from o-$C_6H_4(AsMe_2)_2$ [19, 20] (das) and *cis*-$Me_2AsCH{=}CHAsMe_2$ [21] (*cis*-edas) which do not give planar 1:1 complexes by direct reaction. The 1:1 complexes of dasp are markedly different. The $[Ni(dasp)X_2]$ (X = Cl, Br) are green solids which dissolve in dichloromethane to form purple solutions which soon begin to decompose. These purple solutions exhibit one broad absorption in their electronic spectra at 18.0–18.7 $\times$ 10^{-3} cm^{-1} and this, coupled with their non-conducting properties, suggests that they contain planar $NiAs_2X_2$ chromophores. In contrast, their solid reflectance spectra show absorptions (Table) characteristic of pseudooctahedral nickel(II) [22], and their magnetic moments of 3.25 B.M. (Cl) and 3.20 B.M. (Br) are in the range expected for pseudooctahedral divalent nickel complexes. In support of this stereochemistry is the fact that $Ni(dasp)Cl_2$ exhibits ν(Ni–Cl) at 240 and 230 cm^{-1}, absorptions which are too low for terminal nickel–chlorine stretching vibrations, but not inconsistent with bridging chlorines. Thus, we assign an octahedral structure of type (I) to these compounds in the solid state. These two dasp complexes are rare examples of octahedral nickel(II) with diarsine ligands – other examples being Ni(*cis*-edas)Cl_2 [21] and Ni$\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2$ (X = Cl, Br) [22]. In contrast, the dark brown $Ni(dasp)I_2$ complex appears to have a pseudotetrahedral structure in the solid state as evidenced by its reflectance spectrum; its magnetic moment, μ_{eff} = 2.98 B.M., is consistent with a tetrahedral complex containing ligands well separated in the spectrochemical series



(I)

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*CNS does not specify either *N*- or *S*-bonding.

TABLE. Analyses and Physical Data for the Complexes.

Compound	Colour	Analyses[a]		Λ_M[b]	μ_{eff}(B.M.)	Electronic Spectra ($\times 10^{-3}$ cm^{-1})		Infrared (cm^{-1})
		%C	%H			Dichloromethane	Solid Reflectance	
[Pd(dase)Cl$_2$]	Yellow	35.8(35.6)	4.3(3.7)	<1	diamag.	29.0sh(3,180)	28.0sh	290, 275 ν(Pd–Cl)
[Pd(dase)Br$_2$]	Yellow	30.6(30.6)	3.3(3.2)	<1	diamag.	26.4(4,680)	25.8	240, 215 ν(Pd–Br)
[Pd(dase)I$_2$]	Orange–Brown	26.4(26.6)	3.2(2.8)	<1	diamag.	23.5sh(3,010), 27.5(4,810)	25.0, 20.2sh	
[Pd(dase)(NCS)(SCN)] [c]	Yellow	37.8(37.1)	3.3(3.4)	<1	diamag.	25.5sh(1,740)	24.7	2110, 2070 ν(CN)
[Pd(dasp)Cl$_2$]	Yellow	37.0(36.9)	4.2(3.9)	<1	diamag.	28.4(3,770)	25.0sh	295, 280 ν(Pd–Br)
[Pd(dasp)Br$_2$]	Yellow	31.8(31.8)	3.6(3.4)	<1	diamag.	26.3(3,280)	24.3sh	235, 215 ν(Pd–Br)
[Pd(dasp)I$_2$]	Orange	28.1(27.8)	3.1(3.0)	<1	diamag.	22.4(3,720)	23.0, 20.0sh	
[Pd(dasp)(NCS)(SCN)] [d]	Yellow	37.8(38.1)	3.9(3.7)	<1	diamag.	25.0sh(2,365)	24.7sh	2105, 2080 ν(CN)
[Ni(dase)Cl$_2$]	Red	38.9(39.2)	4.3(4.0)	23	diamag.	19.4[e]	21.5	287, 273 ν(Ni–Cl)
[Ni(dase)Br$_2$]	Red	34.1(34.5)	4.0(3.4)	22	diamag.	26.5sh(512), 18.9(554)	24.8sh, 20.6	230, 210 ν(Ni–Br)
[Ni(dase)I$_2$]	Red–Brown	28.7(28.4)	3.2(2.9)	24	diamag.	27.1(3,470), 17.9(1,070)	19.6, 18.1sh	
[Ni(dase)(NCS)$_2$]	Pink–Brown	40.1(40.0)	3.9(3.7)	28	diamag.	20.5[e]	20.6	2070 ν(CN)
[Ni(dase)$_2$] (ClO$_4$)$_2$	Yellow	38.6(39.1)	4.2(4.1)	171	diamag.	24.0(1,120)	24.1	1080, 620 ClO$_4^-$
[Ni(dase)$_2$Cl] ClO$_4$	Red	41.8(41.9)	4.7(4.4)	89	diamag.	20.2(970)	20.6	1080, 620 ClO$_4^-$
[Ni(dase)$_2$Br] ClO$_4$	Red	40.2(39.9)	4.6(4.2)	91	diamag.	20.1(1,106)	20.3	1080, 620 ClO$_4^-$
[Ni(dase)$_2$I] ClO$_4$	Red–Brown	37.6(38.1)	4.2(4.0)	85	diamag.	19.5(1,200)	20.0	1080, 620 ClO$_4^-$
[Ni(dase)$_2$(NCS)] ClO$_4$	Pale Red	41.4(42.0)	4.6(4.2)	97	diamag.	20.2(1,480)	20.3	2070, 1080, 620
[Ni(dasp)Cl$_2$]	Green	39.4(40.3)	4.6(4.3)	e	3.25	18.7[e]	27.4sh, 15.8, 10.0, 8.6sh	240, 230 ν(Ni–Cl)
[Ni(dasp)Br$_2$]	Gray–Green	33.0(33.5)	3.9(3.7)	e	3.20	18.0[e]	26.7, 18.5, 15.4, 9.5, 8.3sh	
[Ni(dasp)I$_2$]	Brown	30.5(29.8)	3.8(3.2)	e	2.98	17.1[e]	24.0sh, 17.2, 14.1, 11.6	
[Ni(dasp)(NCS)$_2$] [f]	Brown–Purple	42.7(41.4)	4.6(4.4)	30	diamag.	20.4(800)	20.3	2078 ν(CN)
[Ni(dasp)$_2$] (ClO$_4$)$_2$	Brown	39.4(40.1)	5.1(4.4)	183	diamag.	22.8(2,330)	23.0	1080, 620 ClO$_4^-$
[Ni(dasp)$_2$Cl] ClO$_4$	Blue–Black	43.1(43.1)	4.7(5.1)	89	diamag.	26.2(7,220), 16.5(703)	27.4, 19.4, 17.4, 15.5, 13.0sh	1080, 620 ClO$_4^-$
[Ni(dasp)$_2$Br] ClO$_4$	Blue–Black	41.4(41.2)	4.8(4.4)	84	diamag.	25.6sh(3,870), 16.3(864)	27.0, 19.6, 17.3, 15.7, 13.5sh	1080, 620 ClO
[Ni(dasp)$_2$I] ClO$_4$	Blue–Black	38.5(39.2)	4.5(4.5)	80	diamag.	28.8sh(6,570), 15.8(970)	23.3, 17.4, 15.5, 12.8sh	1080, 620 ClO$_4^-$
[Ni(dasp)$_2$(NCS)] ClO$_4$ [g]	Blue–Black	43.3(43.3)	5.1(4.5)	95	diamag.	20.0(1,103)	27.4, 20.0, 17.6, 15.4, 13.4sh	2080, 1080, 620
Ni$_2$(dasp)$_3$(NCS)$_4$ [h]	Brown	43.9(44.6)	4.5(4.5)	insol.	0.40[i]	34.4, 20.7	22.0	2115, 2090, 2070
[Co(dase)$_2$] [CoCl$_4$]	Green	39.6(39.2)	4.2(4.0)	72	2.71[j]	28.1(36.080), 23.8(9.600), 16.6(296), 15.5sh(400), 14.2(490), 6.5(55)	24.4, 16.4sh, 15.0br, 6.4	~300br ν(Co–Cl)
[Co(dase)$_2$] [CoBr$_4$]	Yellow–Green	33.4(33.1)	3.7(3.4)	69	2.70[j]	27.3(23,700), 22.2(5,540), 15.9(160), 15.2sh, 14.6(360), 14.0(450), 6.3(68)	26.7sh, 21.7, 15.5sh, 13.8, 6.3	~230br ν(Co–Br)

[Co(dase)$_2$][CoI$_4$]	Brown	28.6(28.4)	3.0(2.9)	76	2.74[j]	26.5br(22,800), 19.9(4,900) 17.0sh(723), 14.0(360), 12.8(568), 6.1(78)	27.0br, 23.5sh, 19.4 13.9sh, 12.8, 6.1		
[Co(dase)$_2$](ClO$_4$)$_2$	Red	39.0(39.1)	4.4(4.1)	172	2.10	27.5sh, 19.9(3,220), 17.0sh(397), 13.5(92), 9.0(56)	27.0sh, 24.4sh, 19.6, 17.2sh, 13.8sh, ~9.5br	1090,	622 ClO_4^-
[Co(dasp)Cl$_2$]	Green	39.8(40.3)	4.5(4.3)	31	4.20	27.6(8,900), 16.8(424), 14.8(415), ~6.0(60)	25.8, 15.7, 14.6, ~6.1	320br	ν(Co–Cl)
[Co(dasp)Br$_2$]	Brown	34.4(34.5)	3.9(3.7)	29	4.28	24.7(8,100), 14.6sh, 14.0(440), 13.7sh, ~6.0(80)	21.7sh, 15.9, 14.3, 13.5, ~6.0	250br	ν(Co–Br)
[Co(dasp)I$_2$]	Brown	30.2(29.8)	3.6(3.2)	29	4.36	26.0(7,050), 19.2(3,800) 16.0(710), 14.3(700), 13.1sh, 12.2sh, ~5.5(100)	20.8, 19.4, 16.2, 13.9br, 12.8, 6.2		

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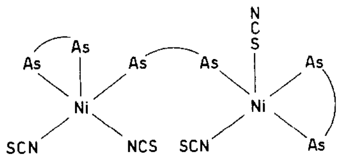
[a] Found(Calculated). [b] Ohm^{-1} cm^2 M^{-1}, 10^{-3} M solutions in MeNO$_2$. [c] Nitrogen, 4.2(4.6). [d] Nitrogen, 4.4(4.8). [e] Decomposes. [f] Nitrogen, 4.9(5.0). [g] Nitrogen, 1.6(1.5). [h] Nitrogen, 4.1(3.8). [i] Moment per Ni atom. [j] Moment for the cation.

which reduces the magnitude of the orbital contribution. It is only slightly soluble in acetone or dichloromethane and decomposes in nitromethane or DMF. The dichloromethane solution exhibits one broad visible absorption band at ~17 × 10^{-3} cm^{-1}, but the poor solubility and tendency to decomposition in solution prevented any study of tetrahedral⇌planar isomerism.

The $Ni(dasp)(NCS)_2$ complex is diamagnetic and the visible spectrum (Table) in both the solid state and solution consists of one broad band at 20.4 × 10^{-3} cm^{-1}, and it thus resembles the $Ni(dase)(NCS)_2$ complex. The IR spectrum in Nujol mull contains one band at 2078 cm^{-1} assignable to $\nu(CN)$ of N-bonded thiocyanate [23]. Unlike $Ni(dase)(NCS)_2$, however, this dasp complex decomposes on recrystallisation producing $Ni(NCS)_2$ and a brown solid which analyses as $Ni_2(dasp)_3(NCS)_4$. It is noteworthy that Cloyd and Meek [5] were able to form a complex of stoichiometry $Ni_2L_3(NCS)_2(BF_4)_2$ with $Me_2PCH_2CH_2CH_2PMe_2$. The $Ni_2(dasp)_3(NCS)_4$ is essentially diamagnetic, μ_{eff} = 0.4 B.M./Ni, and once isolated is only slightly soluble in organic solvents. In the solid state one visible absorption at ~22.0 × 10^{-3} cm^{-1} suggests an essentially square pyramidal structure, and thus a formulation such as $[Ni(dasp)_3][Ni(NCS)_4]$ is excluded. In both dichloromethane and Nujol mull the IR spectrum contains three $\nu(CN)$ absorptions (Table), consistent with two different N-bonded environments and one S-bonded environment. Neither bridging –NCS– or ionic NCS^- groups are present. As the visible absorption band is fairly symmetrical it is likely that each nickel atom is in a fairly similar environment. A structure such as (II) incorporates all these features, though the actual structure may differ in slight detail.



(II)

Both dase and dasp form biscomplexes, $[NiL_2](ClO_4)_2$, which show no evidence of perchlorate coordination in the mull IR spectra (ν_3 is unsplit at ~1080 cm^{-1}) [24] and are 1:2 electrolytes in 10^{-3} *M* nitromethane. Their electronic spectra differ slightly (Table), once again reflecting the greater ligand field strength of the five-membered chelate.

The pentacoordinate $[NiL_2X]ClO_4$ complexes show interesting differences between dase and dasp. The $[Ni(dase)_2X]ClO_4$ (X = Cl, Br, I, NCS) complexes are diamagnetic 1:1 electrolytes, which both in dichloromethane solution and in the solid state have very similar electronic spectra, characteristic of square pyramidal geometry [10, 18, 25]. The IR spectra confirm that the perchlorate groups are ionic. In contrast, the reflectance spectra of $[Ni(dasp)_2X]ClO_4$ (X = Cl, Br, I, NCS) show a number of broad ill-defined absorptions at 20–13 × 10^{-3} cm^{-1} which may be due to a distorted structure between square pyramidal and trigonal bipyramidal. These complexes produce deep blue–green solutions in dichloromethane which exhibit one slightly asymmetric absorption at 15–16 × 10^{-3} cm^{-1}, clearly indicative of trigonal bipyramidal geometry [26, 27]. Further contrast is seen in the $[Ni(dasp)_2(NCS)]^+$ cation, the visible spectrum of which contains one band at 20.4 kK in dichloromethane, in the range expected for square pyramidal nickel(II) species. The difference between the halide and thiocyanate complexes of dasp may be due to the greater ligand field produced by the latter, since the square pyramid is favoured over the trigonal bipyramid on LFSE grounds [28]. The fact that in the solid state $[Ni(dasp)_2(NCS)]ClO_4$ (Table) appears to have a similar structure to the halides, but differs in solution, indicates that the energy difference between the two structures is small. It can thus be seen that while C_2 ligand backbones favour the square pyramidal geometry the longer C_3 linkage can accommodate either square pyramidal or trigonal bipyramidal structures and, further, that the structure adopted by a particular nickel(II) complex in the case of the C_3 ligand is influenced by other ions present and the physical state of the complex.

Cobalt(II) Complexes

Cobalt(II) perchlorate readily forms an orange–red $[Co(dase)_2](ClO_4)_2$ complex on reaction with dase in n-butanol, but all attempts to isolate the analogous compound with dasp failed. The successful isolation of $[Co(bidentate)_2](ClO_4)_2$ complexes depends critically on the ligand – thus C_2 ligands dpe [29], vpp [30] and das [31] readily form complexes of this type, but the corresponding compounds of C_1, $Ph_2PCH_2PPh_2$, and C_3, $Ph_2PCH_2CH_2CH_2PPh_2$, ligands have not been obtained [32]. In nitromethane $[Co(dase)_2](ClO_4)_2$ is a 1:2 electrolyte and it exhibits an electronic spectrum similar to those of other planar cobalt(II) perchlorate complexes [30, 32]. The magnetic moment (2.1 B.M.) is rather low for planar cobalt(II) (accepted range 2.3–2.9 B.M. [33]), but corresponds closely to that reported for monoclinic $[Co(das)_2](ClO_4)_2$ (2.00 B.M.) [31]. In contrast to the latter, however, it shows no evidence of perchlorate interaction in the mull IR spectrum – the $\nu_3(ClO_4)$ band is unsplit at 1090 cm^{-1}.*

Cobalt(II) halides readily form complexes of empirical formula $Co(dase)X_2$ (X = Cl, Br, I). These

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*There is some doubt about the nature of the "orthorhombic" form [31] of $[Co(das)_2](ClO_4)_2$, for which no Co–$OClO_3$ interaction was reported – G. A. Rodley, personal communication.

complexes have effective magnetic moments of 3.4–3.8 B.M./Co atom, thus indicating formulations of type [Co(dase)$_2$] [CoX$_4$]. On this formulation the magnetic moment of the cation approximates to ~2.7 B.M., consistent with planar cobalt(II) (the μ_{eff} values calculated for the cation depends critically upon the values assumed for the CoX_4^{2-} anions, for which a fairly wide range of values are quoted [34]). In support of this formulation the far IR spectra exhibit ν(Co–X) vibrations (Table) consistent with the presence of CoX_4^{2-} anions [35]. In solution the conductivities are low for di-divalent electrolytes and the electronic spectra also show some differences from the reflectance spectra and from spectra reported for the CoX_4^{2-} ions [36], suggesting that dissolution is accompanied by isomerism

$$[Co(dase)_2]\,[CoX_4] \rightleftharpoons 2[Co(dase)X_2]$$

the equilibrium shifting completely to the left on crystallisation. Similar equilibria have been reported previously [32, 38, 39]. The dasp analogues, in contrast, have effective magnetic moments (Table) indicating pseudotetrahedral [Co(dasp)X$_2$] in the solid state. Similar pseudotetrahedral species appear to be present in solution, the small but significant conductivities are probably attributable to solvolysis rather than ionisation due to the presence of an equilibrium of the type found for the dase compounds (solvolysis would be expected to be greater for the sterically encumbered six-membered chelate ring in dasp complexes than in the dase analogues). The apparent inability to form $[Co(dasp)_2]^{2+}$ ions with CoX_4^{2-} anions parallels the failure to isolate this cation with perchlorate counterions. The underlying factors may well be steric in origin, though we have insufficient data from which to draw firm conclusions.

The reactions of dase and dasp with CoX$_2$ salts in a 2:1 molar ratio yielded yellow or brown complexes which, on the basis of analytical, magnetic, and electronic spectral data appear to be mixtures of CoL$_2$X$_2$ and [CoL$_2$X]$_2$[CoX$_4$]; even starting with equimolar CoX$_2$/Co(ClO$_4$)·6H$_2$O, a method used with success by Dyer and Meek [39], no pure complexes could be obtained.

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