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Structural Effects of Chelate Chain Length in High-Spin Nickel(II) Complexes of Triamines

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Bis(3-methylaminopropyl)methylamine (Me$_3$*dpt) forms high-spin five-coordinate [Ni(Me*$_3$*dpt)X*$_2$*] (X = Cl, Br, NCS, NO*$_3$*) and the hydroxo-bridged [Ni(Me*$_3$*dpt)OH]*$_2$*(ClO*$_4$*)*$_2$*. Bis(2-methylaminoethyl)methylamine (Me*$_3$*dien), a structurally analogous ligand, yields pseudooctahedral [Ni(Me*$_3$*dien)*$_2$*]Y*$_2$ *(Y = I, ClO*$_4$*), [Ni(Me*$_3$*dien)(NO*$_3$*)*$_2$*], containing both mono- and bidentate nitrato groups, and [Ni(Me*$_3$*dien)X*$_2$*] (X = Cl, Br, NCS) which are X-bridged dimers in the solid state. The [Ni(Me*$_3$*dien)(NCS)*$_2$*] remains six-coordinate in solution, but the halides yield conducting solutions the electronic spectra of which suggest some five-coordinate species are present. Some dipropylenetriamine analogues are described and the factors influencing the occurrence of five-coordination with triamine ligands are discussed.*

Introduction

Small changes in ligand geometry can, in certain borderline cases, profoundly alter the structure and properties of the corresponding metal complexes. Numerous studies over the past twenty years have identified several such regions in nickel(II) coordination chemistry and have established the approximate ligand geometries and donor sets at which the changes occur [1]. The subtle interplay of steric and electronic factors in borderline cases is still incompletely understood.

The ability of moderately bulky triamines, L, to form high-spin five-co-ordinate [NiLX$_2$] (X = halogen), whilst analogues with smaller steric requirements yield pseudooctahedral [NiLX$_2$]$_n$, has been known for some years [2–4]. In the series of ligands listed here, dien [5] itself yields [Ni(dien)$_2$]$^{2+}$ and [Ni(dien)(H$_2$O)$_3$]$^{2+}$, both octahedral monomers, and Medien [6] yields octahedral polymers of type [Ni(Medien)X$_2$]$_n$. The more bulky Me$_5$-dien [7] produces five-co-ordinate [NiLX$_2$], whilst Et$_4$dien [8] yields planar four-co-ordinate [NiLX]$^+$ which do however exist in equilibrium with five-co-ordinate [NiLX$_2$] in solution. Interestingly, [Ni(Et$_4$-dien)(NCS)$_2$]$_n$ is an –SCN– bridged pseudooctahedral polymer [9]. Longer interdonor linkages as in Medpt also favour five-co-ordination [10]. We have

	R	*R*^{1}	*R*^{11}	*Ligand*
RN(CH$_2$CH$_2$NR^{1}R^{11})$_2$	H	H	H	diethylenetriamine dien
	Me	H	H	bis(2-aminoethyl)methylamine Medien
	Me	Me	H	bis(2-methylaminoethyl)-methylamine Me$_3$dien
	Me	Me	Me	bis(2-dimethylaminoethyl)methylamine Me$_5$dien
	H	Et	Et	bis(2-diethylaminoethyl)-amine Et$_4$dien
RN(CH$_2$CH$_2$CH$_2$NR^{1}R^{11})$_2$	H	H	H	dipropylenetriamine dpt
	Me	H	H	bis(3-aminopropyl)-methylamine Medpt
	Me	Me	H	bis(3-methylaminopropyl)-methylamine Me$_3$dpt

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TABLE I. Physical Properties and Analytical Data for the Complexes.

Compound	Colour	Analysis %[a]				μ_{eff} B.M.[b]	Λ_M[c]
		C	H	N	X		
$[Ni(Me_3dien)Cl_2]_2$	light green	30.9(30.6)	7.1(6.9)	15.2(15.3)	27.9(27.8)	3.00	80
$[Ni(Me_3dien)Br_2]_2$	green	23.3(23.1)	5.3(5.2)	11.8(11.5)		3.27	80
$[Ni(Me_3dien)_2]I_2$	pale blue	28.2(27.9)	6.5(6.4)	13.6(13.9)		2.97	150
$[Ni(Me_3dien)_2](ClO_4)_2$	pale blue	31.0(30.7)	7.1(6.9)	15.5(15.4)		2.99	212
$[Ni(Me_3dien)(NCS)_2]_2$	grey-green	33.9(33.8)	6.2(5.9)	21.7(21.9)		3.10	9
$[Ni(Me_3dien)(NO_3)_2]$	blue	25.9(25.6)	6.0(5.8)	21.6(21.3)		3.11	3
$[Ni(Me_3dpt)Cl_2]$	deep green	35.9(35.6)	7.8(7.6)	13.8(13.9)		3.23	2
$[Ni(Me_3dpt)Br_2]$	green	27.3(27.6)	5.8(5.9)	10.9(10.7)	39.8(40.8)	3.31	1
$[Ni(Me_3dpt)(NCS)_2]$	deep green	38.0(37.9)	6.7(6.6)	20.7(20.1)		3.29	5
$[Ni(Me_3dpt)(NO_3)_2]$	deep green	30.8(30.3)	6.5(6.5)	20.1(19.7)		3.27	3
$[Ni(Me_3dpt)(OH)]_2(ClO_4)_2$	green	30.9(31.0)	6.7(6.9)	11.8(12.1)		3.41	192
$[Ni(dpt)_2]Cl_2 \cdot H_2O$	pale violet	35.1(35.2)	9.4(8.9)	20.1(20.4)		3.02	
$[Ni(dpt)_2]Br_2 \cdot H_2O$	pale violet	29.6(28.9)	7.3(7.3)	17.1(16.8)		3.00	141
$[Ni(dpt)_2]I_2$	blue-violet	25.3(25.1)	5.9(6.0)	14.9(14.6)		2.99	144
$[Ni(dpt)_2](NCS)_2$	blue-violet	38.2(38.5)	7.9(7.8)	25.9(25.6)		3.00	138
$[Ni(dpt)Br_2]_2$	pale green	21.4(20.6)	4.9(4.9)	12.6(12.0)		2.98	
$[Ni(dpt)I_2]_2$	green	17.5(17.3)	4.4(3.9)	9.7(9.5)		2.96	

[a] Found (calculated). [b] ±0.05 B.M. [c] Freshly prepared 10^{-3} M $MeNO_2$ solution.

recently been examining the effects of replacing dimethylene by trimethylene backbones in a variety of bi- and tetradentate ligands [11], and in view of the above results a comparison of the nickel(II) complexes of Me_3dien and Me_3dpt appeared to be of interest. Our results are communicated below.

Results and Discussion

The reaction of Me_3dpt with nickel(II) salts in a 2:1 molar ratio yields only the 1:1 complexes $[Ni(Me_3dpt)X_2]$ (X = Cl, Br, NCS, NO_3) as deep green crystalline solids. All have magnetic moments in the range 3.0–3.3 B.M. and are non-electrolytes in freshly prepared 10^{-3} M nitromethane solution (Table I). Their electronic spectra in the solid state and in solution (Table II) are very similar to those of the five-coordinate Me_5dien complexes [7], and are thus assigned similar structures. In support of this the thiocyanate derivative exhibits a broad adsorption at 2090 cm^{-1}, assignable to ν(CN) of terminal N-bonded isothiocyanato groups [12]. Similarly, in the infrared spectrum of $[Ni(Me_3dpt)(NO_3)_2]$ bands at 1310, 817 and 730 cm^{-1} can be taken as evidence for monodentate nitrato groups [13]. The solution electronic spectrum of $[Ni(Me_3dpt)(NO_3)_2]$ does show small differences to the solid state spectrum, which may indicate some solvolysis. The reaction of Me_3dpt with $Ni(H_2O)_6(ClO_4)_2$ in ethanol containing 2,2-dimethoxypropane as a dehydrating agent yields a green crystalline solid which exhibits infrared bands at 1090 and 620 cm^{-1}, assignable to ionic perchlorate, and a very sharp band at 3630 cm^{-1} assignable as ν(OH). Taken together with the analytical data this indicates a composition $\{[Ni(Me_3dien)(OH)]ClO_4\}_n$, and since the electronic spectra are very similar to the five-coordinate halide complexes, this complex is thus formulated as the hydroxo-bridged dimer (n = 2). A comparison of the solid state electronic spectra of the Me_3dpt complexes shows the expected spectrochemical series as the anion is changed in the order NCS > OH > NO_3 > Cl > Br.

The Me_3dien complexes exhibit more complicated behaviour. The reaction of the appropriate nickel(II) salt and Me_3dien in a 1:2 metal:ligand ratio yield $[Ni(Me_3dien)_2]Y_2$ (Y = I, ClO_4) and $Ni(Me_3dien)X_2$ (X = Cl, Br, NCS, NO_3). Attempts to prepare a 1:1 complex with nickel(II) iodide did not prove successful. The $[Ni(Me_3dien)_2]Y_2$ (Y = I, ClO_4) are 1:2 electrolytes in 10^{-3} M nitromethane and their electronic spectra (Table II) are consistent with NiN_6^{2+} chromophores. The infrared spectrum of $[Ni(Me_3dien)_2](ClO_4)_2$ exhibits the characteristic vibrations (ν_3, ν_4) of ionic perchlorate groups [14] and shows very weak absorptions at ~3600, ~1600 cm^{-1} indicative of some lattice water (*cf.* $[Ni(dien)_2](ClO_4) \cdot ½H_2O$ [6]), although our analytical data suggest that the amount is quite small. The $[Ni(Me_3dien)(NCS)_2]_2$ exhibits a broad absorption at 2090 cm^{-1} and a distinct shoulder at 2130 cm^{-1} consistent with isothiocyanato and bridging thiocyanato groups respectively [12], indicating that the nickel(II) is pseudooctahedrally co-ordinated. The $[Ni(Me_3dien)(NO_3)_2]$ also contains six-co-ordinate nickel(II), on the evidence of its electronic spectrum. The infrared

TABLE II. Electronic Spectral Data.

Compound		$E_{max}(\epsilon_{mol}) \times 10^{-3}$ cm^{-1}
$[Ni(Me_3dien)Cl_2]_2$	$(MeNO_2)$	25.7(56), 18.3sh, 15.7(28), 12.0(2), 9.0(22)
	(d.r.)	25.9, 15.4, 11.7, 9.35
$[Ni(Me_3dien)Br_2]_2$	$(MeNO_2)$	24.1(84), 18.5(28), 15.5(48), 8.4(14)
	(d.r.)	24.7, 18.2, 14.9, 11.0sh, 8.85, 5.2
$[Ni(Me_3dien)_2]I_2$	$(MeNO_2)$	26.4(66), 16.4(16), 12.6(5), 9.2(12)
	(d.r.)	26.7, 17.1, 12.0sh, 9.9
$[Ni(Me_3dien)_2](ClO_4)_2$	$(MeNO_2)$	26.5(79), 16.4(18), 12.6(6), 9.5(16)
	(d.r.)	27.5, 17.4, 12.2sh, 10.1
$[Ni(Me_3dien)(NCS)_2]$	(MeCN)	27.6(80)sh, 17.25(29), 12.6(13)sh, 10.4(36)
	(d.r.)	26.7sh, 16.7, 13.3sh, 9.8
$[Ni(Me_3dien)(NO_3)_2]$	(MeCN)	27.4(41), 17.15(20), 12.3(7)sh, 10.4(16)
	(d.r.)	27.2, 16.7, 12.4sh, 10.0
$[Ni(Me_3dpt)Cl_2]$	(CH_2Cl_2)	24.85(197), 18.95(3)sh, 14.9(59), 12.5(10)sh, 11.4(5), 7.65(11), 4.6(10)
	(d.r.)	24.7, 18.85, 14.8sh, 12.5sh, 11.1sh, 7.7, 4.4
$[Ni(Me_3dpt)Br_2]$	(MeCN)	24.4(388), 14.55(81), 7.75(14), 4.6(5.5)
	(d.r.)	24.3, 18.2, 14.3, 7.8, 5.85, 4.35
$[Ni(Me_3dpt)(NCS)_2]$	(MeCN)	25.5(468), 15.7(82), 9.55(15)sh, 7.65(5), 5.25(35)
	(d.r.)	25.8, 22.2sh, 19.3sh, 15.75, 12.75sh, 7.8, 5.7, 4.4
$[Ni(Me_3dpt)(NO_3)_2]$	(MeCN)	27.4(58), 16.8(27), 12.65(6)sh, 9.8(9), 4.9(7)
	(d.r.)	25.8, 15.5, 12.4, 9.05, 5.8, 4.9, 4.4
$[Ni(Me_3dpt)(OH)]_2(ClO_4)_2$	$(MeNO_2)$	25.65(124), 15.3(49), 12.4(24), 7.1(18), 5.3(9)
	(d.r.)	26.1, 21.9, 15.85, 12.7, 11.7, 7.6, 5.8, 4.3
$[Ni(dpt)_2]Cl_2\cdot H_2O$	(d.r.)	28.8, 17.9, 10.8
$[Ni(dpt)_2]Br_2\cdot H_2O$	(d.r.)	28.8, 18.0, 10.8
$[Ni(dpt)_2]I_2$	(d.r.)	28.8, 17.7, 10.7
$[Ni(dpt)_2](NCS)_2$	(d.r.)	28.8, 17.7, 10.9
$[Ni(dpt)Br_2]_2$	(d.r.)	26.5, 15.5, 10.2
$[Ni(dpt)I_2]_2$	(d.r.)	27.7, 15.2, 9.5
"$Ni(dpt)Cl_2$"	(d.r.)	26.3, 15.8, 10.6

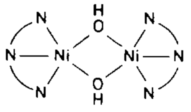
spectrum of this complex is very similar to that of $[Ni(dien)(NO_3)_2]$ [13], which contains both mono- and bidentate nitrato ligands and a $NiN_3O_3^{2+}$ chromophore is no doubt also present in the former.

The structures of the $[Ni(Me_3dien)X_2]_n$ (X = Cl, Br) are more difficult to determine. In the solid state their electronic spectra are similar in profile to $[Ni(Me_3dien)_2]Y_2$ (Table II) and show the shift of E_{max} to lower energy that would be expected for replacement of one triamine ligand by three halide ligands. It is possible that hexaco-ordinate halide-bridged dimers are present (n = 2). However, the $[Ni(Me_3dien)Br_2]$ shows some extra weak electronic spectral absorptions which could indicate the presence of a five-co-ordinate moiety. In solution in nitromethane the complexes exhibit conductances consistent with approximately 1:1 electrolytes, and their electronic spectra resemble in profile those of $[Ni(Me_3dpt)X_2]$, although the ϵ_{mol} values are rather low. The nature of the species present in solution is rather unclear but certainly differs from that present in the solid state. The far-infrared spectra of the chloro and bromo complexes in the solid state are very similar, but since ν(M–X) could not be clearly identified, yield no further evidence about the structures present.

A number of nickel(II) complexes of dipropylenetriamine, bis(3-aminopropyl)amine, have been reported previously *viz.*: $[Ni(dpt)_2]Y_2$ (Y = Cl, NO_3, ClO_4, BF_4), $Ni(dpt)Cl_2$, $[Ni(dpt)(NCS)_2]_2$ and $[Ni(dpt)(NO_3)_2]$ [5, 6, 13, 15, 16], and various of their physical and spectroscopic properties recorded. Several of these and also some new complexes: $[Ni(dpt)_2]Y_2$ (Y = Cl, Br, I, NS) and $[Ni(dpt)X_2]_2$ (X = Br, I) were prepared by us for comparison with the Me_3dpt complexes described above. All of the $[Ni(dpt)_2]Y_2$ exhibit essentially identical electronic spectra, exhibiting bands at ~29, ~18, ~11 × 10^3 cm^{-1}, assignable to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3T_{1g}(F)$ and $^3T_{2g}$ transitions, respectively, in octahedral symmetry.

No pure $Ni(dpt)Cl_2$ could be isolated, but $[Ni(dpt)X_2]$ (X = Br, I, NCS, NO_3) were readily prepared. The results for the isothiocyanato and nitrato complexes are in agreement with those previously reported, and the bromo and iodo complexes have electronic spectra quite consistent with halide-bridged dimers. Thus, no examples of five-coordinate complexes of nickel(II) with dpt seem to exist.

The Me_3dpt ligand produces five-co-ordinate complexes $[Ni(Me_3dpt)X_2]$ in every case examined – there is no evidence for dimerisation *via* X-bridging, or, in the case of X = NO_3, for one of the anions behaving in a bidentate manner. Neither could we isolate a $[Ni(Me_3dpt)_2]^{2+}$ moiety; even for the perchlorate complex the novel hydroxo-bridged $[Ni(Me_3dpt)(OH)]_2(ClO_4)_2$, (I) is formed instead. In marked contrast, all the known dpt complexes contain six-co-ordinate nickel(II). The intermediate Medpt [10] appears also to produce only five-co-ordinate complexes. The Me_3dien complexes appear to be predominantly six-co-ordinate – both $[Ni(Me_3dien)_2]^{2+}$ and dimeric $[Ni(Me_3dien)X_2]_2$ can be isolated, although there is evidence that five-co-ordinate species may occur in solution. The uncertainties are mainly due to the difficulty of distinguishing five- and six-co-ordinate [2, 3, 10] high-spin nickel(II) on the basis of electronic spectral band profiles alone. When ϵ_{mol} values are obtainable the much higher values of the five-co-ordinate complexes provide a ready distinction, but in such cases as the $[Ni(Me_3dien)X_2]_2$ (X = Cl, Br) in solution, where complicated solvolysis appears to occur, the ϵ_{mol} values observed are not so reliable since the species (or number of species) present is unclear.



(I)

Summarising these results, it is seen that five-co-ordination is promoted by increasing backbone length and methyl substitution at the nitrogen – trimethylene (dpt) linkages alone are not sufficient to promote five-co-ordination but a single (Medpt) or three (Me_3dpt) methyl groups in combination are. With dimethylene linkages even three methyl groups (Me_3dien) are insufficient, although the fully alkylated Me_5dien does yield five-co-ordinate complexes [7]. The larger steric requirements of triamines with longer backbones [2, 16] and larger substituents appear to be the determining factor in limiting the coordination number to five.

Experimental

The triamines were purified by distillation from BaO and used as standard solutions in ethanol. Nickel(II) salts were used as purchased and were dehydrated *in situ* by reluxing ethanolic solutions with 2,2-dimethoxypropane (DMP). The preparations of the complexes were generally similar and are illustrated by the following examples:

$[Ni(Me_3dpt)(OH)]_2(ClO_4)_2$

The ligand (2.0 g; 11.6 mmol) was added to a stirring solution of $Ni(H_2O)_6(ClO_4)_2$ (previously dehydrated with DMP) (2.12 g; 5.8 mmol) in ethanol (20 cm^3), and after 1–2 min a green precipitate was deposited. Stirring was continued for 15 min and then the green powder was filtered, washed with ethanol, ether, and dried *in vacuo* of P_4O_{10}. Yield = 1.8 g (90%).

$[Ni(Me_3dien)Cl_2]_2$

The ligand (2.0 g; 13.8 mmol) was added to a stirring solution of $NiCl_2$ (0.90 g; 6.8 mmol), in ethanol (20 cm^3), and the resulting yellow solution was heated to boiling for 5 min during which time a green solution formed. Upon standing in the refrigerator this green solution deposited light green crystals. Recrystallisation was affected from hot acetonitrile. Yield = 1.7 g (84%).

Physical Measurements

These were made as previously described [17].

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