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IV. NOVEL COMPOUNDS

FIVE-COORDINATED COMPLEXES OF *3d* BIVALENT METAL IONS WITH POLYAMINES

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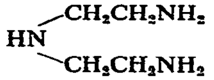
Until a few years ago, complexes of coördination number five for bivalent metals from manganese to zinc were rather rare compared with those for coordination number four or six. In the case of manganese(II) and iron(II) five-coordinated compounds were completely unknown. Cobalt(II)[1] and nickel(II)[2] complexes were all low-spin compounds, with phosphorus or arsenic as donor atoms. Few five-coordinated copper(II) and zinc(II) complexes are known. Very recently, however, Prof. Sacconi and coworkers have described the first examples of five-coordinated high-spin complexes of manganese(II), cobalt(II) and nickel(II)[3-5]. Another five-coordinated zinc complex is also known[3,6]. In his lecture, Prof. Sacconi will also say something about these compounds. Such high-spin configurations occur with ligands containing nitrogen and oxygen as donor atoms[7].

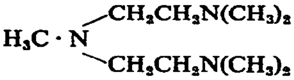
We have now undertaken a systematic investigation of both the preparation and properties of five-coordinated complexes of bivalent *3d* ions with particular interest in high-spin compounds. We believe that suitable ligands are those which fulfill the main conditions: 1) the ligand must be multidentate and sufficiently bulky in order that crowding around the metal should prevent a six coordinated configuration being attained; the donor atoms must possess a strong coordinating ability so that they are all coordinated to the metal; 2) many of the donor atoms must be highly electronegative so that the coordinated bonds are largely ionic in character. Their π-bonding ability must also be weak.

This communication reports data on the metal complexes of two polyamines. One of these is bis(2-dimethylaminoethyl)methylamine, which is a pentamethyl derivative of bis(2-aminoethyl)amine (den). The other ligand is tris(2-dimethyl-



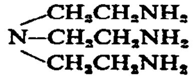
$$\mathrm{HN}\begin{matrix}\diagup CH_2CH_2NH_2\\ \diagdown CH_2CH_2NH_2\end{matrix}$$

den



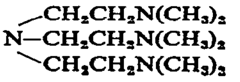
$$H_3C\cdot \mathrm{N}\begin{matrix}\diagup CH_2CH_2N(CH_3)_2\\ \diagdown CH_2CH_2N(CH_3)_2\end{matrix}$$

denMe



$$\mathrm{N}\begin{matrix}\diagup CH_2CH_2NH_2\\ -CH_2CH_2NH_2\\ \diagdown CH_2CH_2NH_2\end{matrix}$$

tren



$$\mathrm{N}\begin{matrix}\diagup CH_2CH_2N(CH_3)_2\\ -CH_2CH_2N(CH_3)_2\\ \diagdown CH_2CH_2N(CH_3)_2\end{matrix}$$

trenMe

aminoethyl)amine, which is a hexamethyl derivative of tris(2-aminoethyl)amine (tren). These ligands have been termed denMe and trenMe, respectively, for short.

Let us first consider the metal complexes of trenMe. This potentially quadridentate ligand forms compounds with the bivalent transition ions, from iron to zinc, of the formula $MX_2 \cdot$ trenMe. As anions, the bromide, chloride, iodide, nitrate and perchlorate ions have been used (Table I). These compounds are soluble in alcohols, nitroethane, nitrobenzene, but are insoluble in non-polar solvents; the halides are also very soluble in chloroform. They are fairly stable to dry air but the ferrous complex oxidizes in a few days.

TABLE I

KNOWN $M(denMe)X_2$ (^{0}) AND [M(trenMe)X]X (*) COMPOUNDS

X	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
Cl	0	*0	*0	*0	0	0
Br	0	0	*0	*0	*0	0
I			*0	*0		
NCS			*0	*0		
ClO_4			*	*	*	*
NO_3				*	*	

With the obvious exception of the zinc complex, all these compounds are of the high-spin type, both in solution and in the solid state (Table II). The orbital contributions to the magnetic moments are fairly small for the cobalt and copper compounds. With the nickel compounds the size of the orbital contribution is intermediate between those found in tetrahedral and octahedral compounds. In all cases the magnetic moments are essentially independent of temperature.

The reflectance spectra of all of the complexes of a given element are very similar in shape, independently of the nature of the anion X. One observes, of course, small shifts of the frequencies at the peaks which can be correlated with the position of the anion in the spectrochemical series. Thus it may be concluded that the same stereochemistry is present in all complexes of a given element, in the solid state.

Moreover, X-ray powder photographs of the complexes of iron, cobalt, nickel, copper and zinc with a given anion are practically identical with one another. This fact leads one to conclude that the same kind of stereochemistry is present in all of these complexes in the solid state.

In all cases the absorption spectra of the solutions of these complexes in chloroform and nitroethane are virtually identical with their solid state spectra. This indicates that no appreciable structural change occurs on dissolution. In particular nitroethane is not appreciably coordinated to the metal. The spectra of [M(trenMe)Cl]Cl complexes both in chloroform solution and in the solid state are shown in Figs. 1–4.

TABLE II

MAGNETIC DATA FOR SOME [M(trenMe)X]X AND M(denMe)X_2 COMPLEXES

Compound	*State*	*t, °C*	$\chi_g \times 10^6$ (c.g.s.)	$\chi_M \times 10^6$ (c.g.s)	μ_{eff} (B.M.)
[Co(trenMe)Cl]Cl	Solid	−194	85.00	30,857	4.43
		−80	35.02	12,851	4.48
		20	23.19	8,590	4.50
[Co(trenMe)Br]Br	$CHCl_3$	22	18.10	8,370	4.47
[Ni(trenMe)Cl]Cl	Solid	−194	48.89	17,836	3.48
		−81	21.48	7,970	3.52
		22	13.03	4,912	3.42
	$CHCl_3$	21	13.03	4,930	3.42
[Ni(trenMe)Br]Br	$CHCl_3$	19	10.44	4,952	3.42
[Ni(trenMe)NO_3]NO_3	Solid	22	10.46	4,540	3.28
[Cu(trenMe)Br]Br	Solid	21	2.68	1,459	1.86
[Cu(trenMe)ClO_4]ClO_4	Solid	21	2.45	1,454	1.86
Mn(denMe)Cl_2	Solid	22	47.64	14,433	5.85
Fe(denMe)Cl_2	Solid	21	37.96	11,390	5.20
Co(denMe)Cl_2	Solid	−164	66.50	23,103	4.50
		−105	49.00	15,038	4.53
		18	28.82	8,919	4.60
Co(denMe)Br_2	$CHCl_3$	25	23.97	9,595	4.80
Ni(denMe)Cl_2	Solid	−193	54.10	16,571	3.27
		−110	26.26	8.136	3.37
		19	15.21	4,769	3.36
	$CHCl_3$	19	15.33	4,826	3.38
Ni(denMe)Br_2	$CHCl_3$	25	11.59	4,744	3.38
Cu(denMe)Cl_2	Solid	20	4.06	1,430	1.84
	$CHCl_3$	25	4.19	1,471	1.88

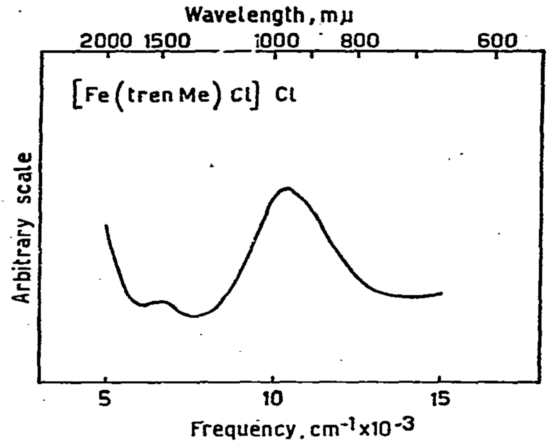


Fig. 1. Reflectance spectrum of [Fe(trenMe)Cl]Cl.

Additional information on the stereochemistry of these complexes is derived from conductivity and molecular weight data (Table III). The conductivity values are typical of uni-univalent electrolytes. Dimerization of the cations *via* bridging

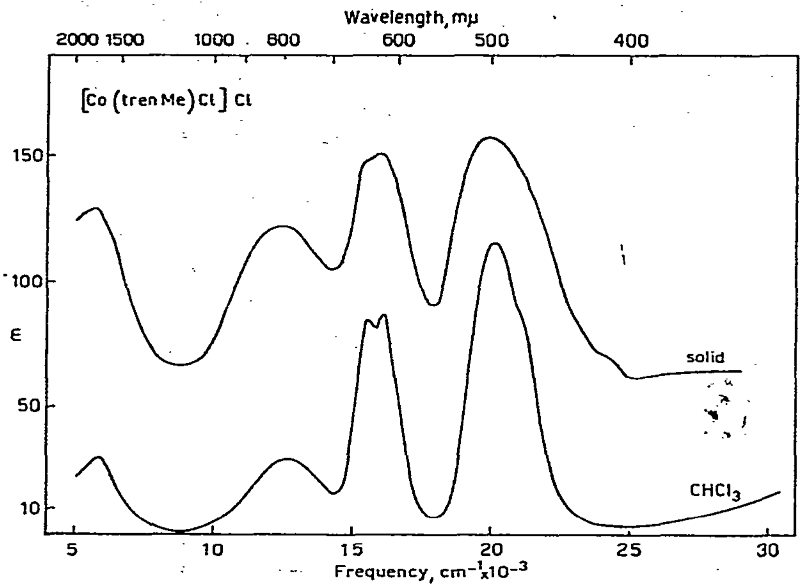


Fig. 2. Solution and solid state spectra of [Co(trenMe)Cl]Cl.

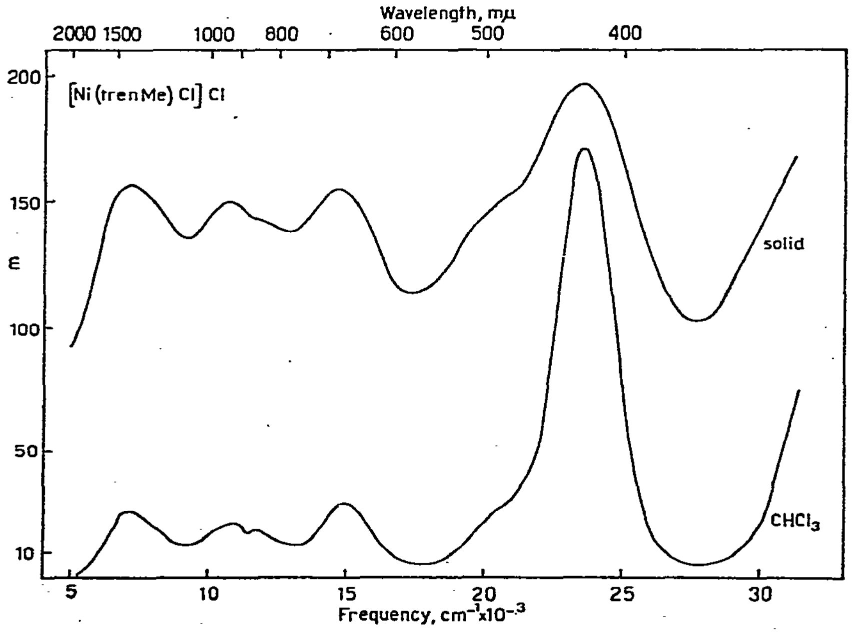


Fig. 3. Solution and solid state spectra of [Ni(trenMe)Cl]Cl.

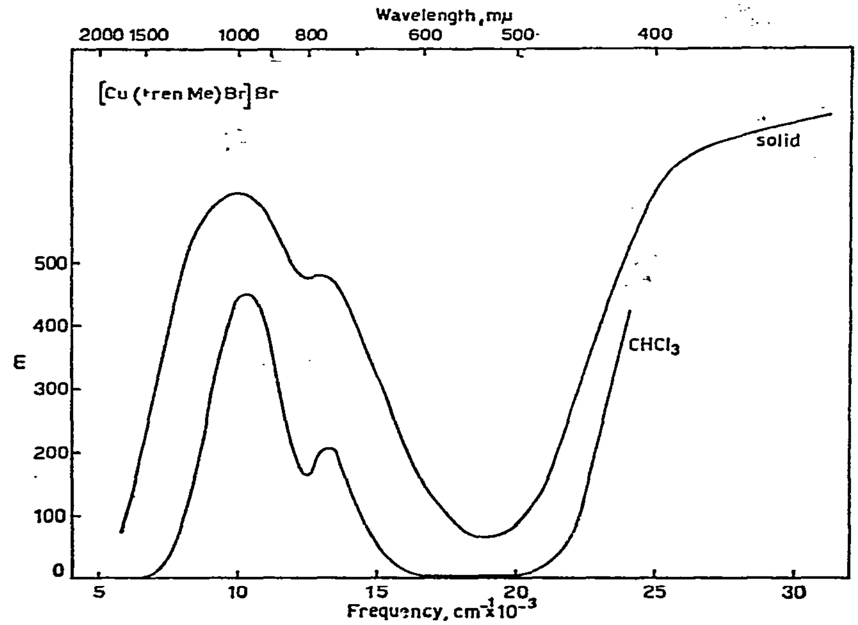


Fig. 4. Solution and solid state spectra of [Cu(trenMe)Br]Br.

TABLE III

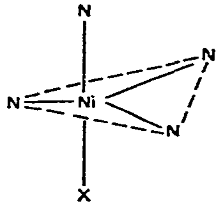
MOLECULAR WEIGHTS AND CONDUCTIVITY DATA OF [M(trenMe)X]X AND M(denMe)X_2 COMPLEXES

Complex	*Molar conductance (cm²/ohm mole)*		*Van 't Hoff coefficient*	
	$C_6H_5NO_2$	$C_2H_5NO_2$	$C_2H_5NO_2$	$CHCl_3$
[Co(trenMe)Cl]Cl	32	80	1.45	
[Co(trenMe)Br]Br	30	83	1.60	
[Co(trenMe)I]I	32	89	1.66	
[Co(trenMe)ClO_4]ClO_4	31	93	1.47	
[Ni(trenMe)Cl]Cl	31	80	1.41	
[Ni(trenMe)Br]Br	32	77	1.47	
[Ni(trenMe)I]I	31	84	1.65	
[Ni(trenMe)ClO_4]ClO_4	26	102	1.55	
[Cu(trenMe)Br]Br	32	79	1.59	
[Cu(trenMe)ClO_4]ClO_4	33	103	1.59	
[Cu(trenMe)NO_3]NO_3	31	83	1.46	
Mn(denMe)Cl_2		2.0	0.96	
Co(denMe)Cl_2		1.1	0.97	1.11
Co(denMe)Br_2		2.7	0.96	1.15
Ni(denMe)Cl_2		2.0	0.92	1.14
Ni(denMe)Br_2		4.9	0.87	1.25
Cu(denMe)Cl_2		16.1	0.78	1.30
Zn(denMe)Cl_2		3.3	0.97	1.10
Zn(denMe)Br_2		4.1	1.01	
Reference Compounds				
[NBu_4]Br	27	70	1.56	
[NBu_4]I	30	83	1.62	
[NEt_4]$_2$[Co(NCS)$_4$]	35	147	1.99	

halides or nitrate ions is to be ruled out on the basis of the molecular weight measurements. Actually a small degree of association is found which is, however, to be ascribed to ion-pair association. Indeed the Van 't Hoff factor, *i*, is 1.41–1.67 based on the monomeric formulation. Values twice as high are of course calculated for the dimeric formula. These values are to be compared with those of reference electrolytes under the same conditions. They are: 1.56–1.62 for the uni–univalent electrolytes but only 1.91–2.30 for the uni–bivalent electrolytes. Thus, it is found that the present compounds behave as uni–univalent electrolytes. Furthermore, the *i* values for the perchlorate compounds are practically the same as those for the other compounds. The perchlorate ion is unlikely to behave as a bridging ligand.

Thus these compounds of trenMe are to be formulated as [M(trenMe)X]X. Since the ligand is potentially quadridentate, this formulation rules out the coordination number six of the metal but not necessarily the coordination number four. This coordination number could occur if a nitrogen atom is not coordinated to the metal. Conclusive evidence concerning the stereochemistry of these complexes is obtained when their spectra are compared with the spectra typical of various high-spin configurations. It is found that the spectra of the trenMe complexes cannot be consistently interpreted in terms of a regular or distorted tetrahedral configuration[8]. Instead, there is a marked similarity with the spectra of some high-spin cobalt and nickel complexes[3,4] for which a five-coordinated structure was proved by X-ray methods[6,9]. Such compounds will be described by Prof. Sacconi in his lecture. The spectra of the trenMe complexes of cobalt and nickel approach more nearly the spectra of the trigonal bipyramidal compounds.

Thus we conclude that these trenMe complexes of the transition elements from iron to copper have a five-coordinated structure both in solution and in the solid state.



Stuart molecular models of the complexes have been constructed and these show that the trigonal bipyramidal structure is indeed the most likely structure to result when all four nitrogen atoms of the ligand are attached to the metal. The geometry of the ligand is such that three dimethylamine groups are constrained to lie at the corners of an equilateral triangle which has the metal atom at the center. There is no room for another ligand in the same plane as the dimethylamino groups, and in this way an octahedral or square pyramidal structure cannot be attained. The only coordination position available, in which there is little steric hindrance, is on the threefold axis of the triangle. This is occupied by the anion.

Let us now consider the complex compounds which are formed by ligand denMe with bivalent transition metal ions from manganese to zinc. They have the stoichiometric formula $MX_2 \cdot$ denMe (Table I). These compounds are hygroscopic solids fairly stable to dry air with the exception of the iron complex which oxidizes in a few weeks. These complexes are all very soluble in alcohols, nitroethane, nitrobenzene and chloroform.

All of the compounds from manganese to copper are of the high-spin type both in solution and in the solid state (Table II). The orbital contributions to the magnetic moments are rather small and almost independent of temperature. A five-coordinated structure is also to be assigned to these denMe complexes. Indeed all of these compounds are non-conducting in chloroform and nitrobenzene solution (Table III). This fact indicates that both the halides are coordinated to the metal. In nitroethane solutions these compounds show a slight conductivity. The conductivity values are in the range 2–5 $ohm^{-1} \cdot mole \cdot cm^2$ that is less than 5% of the values found with uni–univalent electrolytes under the same conditions. The copper compound has a higher conductivity. This slight conductivity is to be ascribed to the partial displacement of the halides by the solvent molecules.

The molecular weights of the non-oxidizable chloro-complexes in chloroform show that the compounds are essentially monomeric in this solvent (Table III). There is, however, a small percentage of associated species (of about 10%). For the copper chloro-compound and nickel bromo-compound the degree of association is higher. In nitroethane, a slight dissociation occurs as it is also shown by conductivity measurements. Hence these complexes are predominantly present in solution as non-ionic monomeric species. These are to be formulated as $[M(denMe)X_2]$. Since denMe is a potentially tridentate ligand, this formulation excludes a six-coordinated structure.

The spectra of these compounds give further evidences in favour of a five-coordinated structure. The absorption spectra of the compounds dissolved in chloroform closely correspond to their reflectance spectra while that of the copper compound in nitroethane is rather different. For a given element the spectra of the chloro, bromo and iodo complexes are very similar. They usually exhibit only small red shifts of the bands on passing from chloro to bromo and iodo derivatives. These spectral data, coupled with the magnetic data, cannot be consistently interpreted in terms of a four-coordinated structure. Instead the spectra of these complexes from iron to copper are similar to those of the high-spin five-coordinated compounds, such as the trenMe complexes. Red shifts of the band frequencies with respect to those of the trenMe complexes are usually found. This fact is expected as the donor set is N_3X_2 in the denMe complexes and N_4X in the trenMe complexes.

All of the above evidences indicate that the compounds from iron to copper have a five-coordinated structure. A definitive confirmation of such a coordination number is provided by a three-dimensional X-ray analysis of the Co(denMe)Cl_2 compound. At the present stage of the investigation the discrepancy factor is about 15%. The structure consists of discrete molecules in which cobalt has a coordination number of five. The stereochemistry exhibited by the metal is intermediate between the trigonal bipyramid and the square-pyramid*.

The same structure must also be attributed to the complexes of the other elements on account of their mutual isomorphism with the cobalt complexes. In particular this conclusion holds true for the manganese and zinc complexes for which the spectral criterion fails.

In conclusion the metal compounds of the ligands denMe and trenMe join the few examples of five-coordinated complexes, particularly those of high-spin. It is interesting to recall that the cobalt(II) and nickel(II) complexes with ligands structurally similar to the present amines but containing arsenic or phosphorus in the place of nitrogen, *e.g.* $CH_3As(CH_2CH_2CH_2As(CH_3)_2)_2$ are all low-spin[1,2]. This is probably because the coordinated bonds are more covalent in character with donor atoms like phosphorus and arsenic than with nitrogen. In fact the electronegativity of the first two elements is very close to that of these metal ions. Also π-bonding may play a part in promoting spin-pairing.

A crystal field model for the spectra of [Co(trenMe)X]X and [Ni(trenMe)X]X

The spectra of the trenMe complexes of cobalt and nickel may be discussed in terms of the crystal field theory. The well-known weak field scheme with configuration interaction has been used[10], spin–orbit coupling being neglected. A crystalline potential of five equal point dipoles of strength μ arranged in a trigonal bipyramidal configuration has been assumed[11]. Strictly, the energy level diagrams so obtained (Figs. 5, 6) are valid for D_{3h} symmetry. However, they may be also used approximately for the trenMe compounds.

The spectra of the cobalt-trenMe complexes exhibit four main absorption bands. The highest energy band is at about 20,000 cm^{-1}. If this band is tentatively assigned to the transition from the ground state to the $^4E''(P)$ state, then the upper states of the three other transitions are (in order of increasing energy): $^4E''(F)$, $^4E'(F)$ and $^4A_2'(P)$. (Fig. 5; $\mu \approx 1.2$ a.u.). This assignment is supported by the smaller field dependence of the frequencies of the first and third bands than the second and fourth bands. The agreement is satisfactory as is shown in Table IV.

The nickel-trenMe complexes exhibit three absorption bands of higher intensities and two weaker bands. The ratio of the frequencies at the peaks of the first two intense bands is about 2.0. The highest energy band falls in the range 22,000–24,500 cm^{-1} and is assigned to the transition from the ground state to the

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* We are indebted to Drs. M. Di Vaira and P. L. Orioli of this laboratory for letting us know the results of the structure analysis before publication.

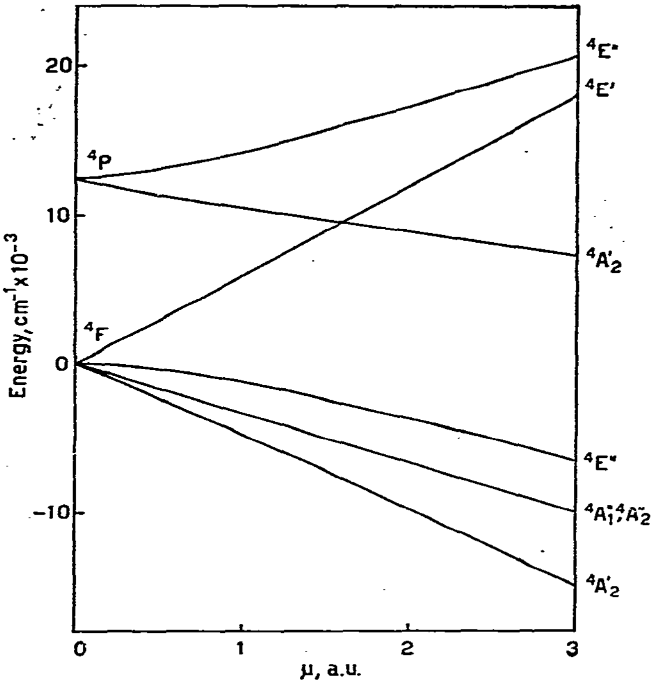

Fig. 5. Energy level diagram for the cobalt(II) ion in fields of five equivalent dipoles of strength μ arranged in a trigonal bipyramidal configuration.

TABLE IV

COMPARISON BETWEEN PREDICTED AND OBSERVED SPECTRA OF [Co(trenMe)Cl]Cl AND [Ni(trenMe)Cl]Cl

Compounds	*Transitions*	*Frequencies, cm^{-1}*	
		calculated	*observed*
[Co(trenMe)Cl]Cl	$^4A_2'(F) \rightarrow {}^4E''(F)$	4,000	5,500
(μ = 1.2 a.u.)	$^4E'(F)$	12,000	12,500
	$^4A_2'(P)$	15,800	15,600–16,100
	$^4E''(P)$	20,000	20,000
[Ni(trenMe)Cl]Cl	$^3E'(F) \rightarrow {}^3E''(F)$	7,000	7,200
(μ = 2.2 a.u.)	$^1E'(F)$	12,900	11,000–12,000 w
	$^3A_1''(F)$; $^3A_2''(F)$	14,000	
	$^3A_2'(F)$	15,300	15,000
	$^1E''(D)$	19.000	≈20,000 sh
	$^3E''(P)$	23,500	23,500
	$^3A_2'(P)$	26,000	≈25,500 sh

level $^3E''(P)$. (Fig. 6; $\mu \approx 2.0$ a.u.). The transition to the level $^3A_2'(P)$ is a two electron jump in the strong field limit and thus it is expected to be weak. The transition to the states $^3A_1''$, $^3A_2''$ (which are degenerate in D_{3h} symmetry) are the

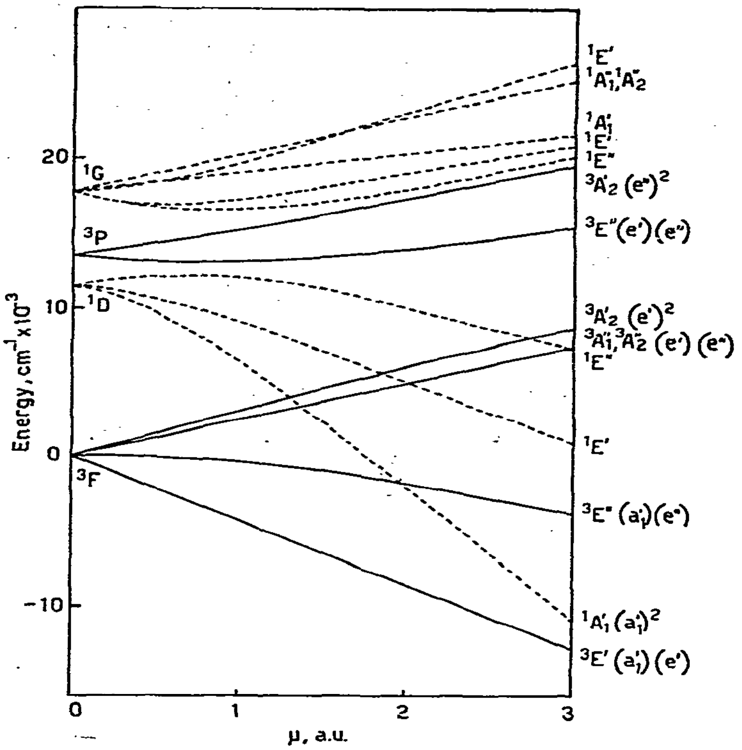

Fig. 6. Energy level diagram for the nickel(II) ion in fields of five equivalent dipoles of strength μ arranged in a trigonal bipyramidal configuration.

only transitions which do not gain intensity *via* mixing of the metal *p* and *d* orbitals. The comparison between the observed and predicted transitions is reported in Table IV for the [Ni(trenMe)Cl]Cl compound. The agreement is found to be satisfactory.

The stereochemistry of some metal complexes of tren and den

It is interesting to recall the results of previous works on the stereochemistry of the complexes of the ligands tren and den, in which the amino groups are, of course, less bulky than those of trenMe and denMe.

At first it was held that the ligand tren could form only tetrahedral complexes[12], but later it was realized that it could more easily form a *cis*-octahedral complex with additional ligands as, for instance, two water molecules, or anions[13]. Then, a thermochemical study showed that species with a coordination number less than six could be present in solution, at least with cobalt and zinc[14]. In the case of nickel, complexes with metal–ligand ratio of 1:1, with various anions, have spectra both in the solid state and in solution characteristic of octahedral configuration, as was so interpreted by Jørgensen[15]. The complex $[Ni(tren)(NCS)_2]$ was then shown to be octahedral by X-ray crystallography[16]. The solution spectra of the copper complexes were considered by Jørgensen to be compatible with six coordination[15]; they are different from the spectra of trenMe complexes of copper, the higher frequency band being absent. The *cis*-octahedral configuration with two molecules of water thus appears to be more likely in this case. On the other hand the spectrum of the complex $[Cu\ tren(OH)]^+$ in alkaline solution[17] (two bands at 11,900 and 14,400 cm^{-1}) is similar to those of the $[Cu(trenMe)X]^+$ complexes. This leads to the assignment of a five coordinated configuration to $[Cu\ tren(OH)]^+$. Finally the case of the cobalt-tren complex, for which a probable high-spin five-coordinated structure has been postulated on the basis of the entropy of formation on the one hand and on spectral evidence on the other[14]; the close similarity of the spectra of the complex ions [Co(trenMe)X]X with that of the tren complex in aqueous solution[14] further supports the assumption of a five coordinated (distorted trigonal bipyramidal) structure for the complex which should be formulated as $[Co(tren)H_2O]^{2+}$. The molar extinction coefficients are about a third of the values for the cobalt-trenMe complexes which could indicate that not all the molecules have the same stereochemistry, weakly absorbing species such as the octahedral species, being present.

One may therefore conclude that the steric requirements of the amine tren are already on the borderline of compatibility for five or six coordination. The five coordinated structure can be attained depending either on the nature of the metal ion (case of cobalt) or on the presence of other suitable ligands in solution, such as the hydroxide ion in the case of the copper-tren complex.

All the ions from manganese(II) to zinc(II) form complexes with the non-methylated amine den of the type $Mden^{2+}$ and $Mden_2{}^{2+}$ in aqueous solution[18,19]. With the possible exception of the compounds of copper and zinc, the others are all octahedral (the first ones through coordination of, say, three molecules of water)[19]. Moreover Bernard and Barclay isolated the compounds $Co\ denCl_2$ and $Co\ denBr_2$ which are high-spin[20]. For these compounds they postulated a structure either of the type (Co denX)X (with cobalt pseudotetrahedral) or of the type $(Co\ den_2)(CoX_4)$ (with tetrahedrally and octahedrally coordinated cobalt present). We have now measured the reflectance spectrum of the $Co\ denCl_2$ compound, between 5000 and 30,000 cm^{-1}. It shows intense bands in the region from 5000–6000 and 14,000–20,000 cm^{-1}, which are characteristic of the $CoCl_4{}^{2-}$ ion, and a weaker band at 10,500 cm^{-1}, which is characteristic of the hexamine-cobalt(II) species. These data lead to the conclusion that the structure, which contains six- and four-coordinated cobalt present at the same time, is more stable than one with a five-coordinated cobalt, when the ligand is den. The opposite is true when the ligand is denMe. It is very likely that this is due to the steric requirements of the methyl groups of the ligand denMe, which cause strong steric hindrance to the coordination of two denMe molecules to the same metal ion. In fact Stuart molecular models of the ion Mden$_2$ cannot be assembled. One must not, however, neglect the fact that there is a high lattice energy contribution to the stabilization of the ionic structure (Coden$_2$)(CoCl$_4$). Unfortunately the insolubility of this compound in inert solvents prevents us from ascertaining if this structure is also maintained in the absence of crystal forces.

In connection with the relative stabilities of the tetrahedral, trigonal-bipyramidal and octahedral structures, Nyholm and Tobe have showed that the disproportionation

$$2MX_5 = MX_4^+ + MX_6^-$$

involves a decrease in energy[21]. This result refers to a purely ionic model, and X is a unidentate charged ligand. In the present case, however, many other factors, should be taken into account.

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