Complexes of Nickel(II) and Copper(II) with some 2,3,4,5-Tetrahydro-1*H*-1,5-benzodiazepines

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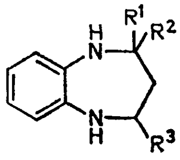
The preparation and characterisation of some nickel(II) and copper(II) complexes with methyl-substituted tetrahydro-1,5-benzodiazepines are reported. Some magnetic properties and electronic and vibrational spectroscopic data are discussed. The nickel perchlorate complexes appear to be square-planar with two diazepine ligands assuming a *trans*-arrangement. The copper perchlorate complex of the trimethylbenzodiazepine is also square-planar but a decrease in the methyl-substitution of the diazepine ligand apparently allows the approach of further co-ordinating species and the formation of five-co-ordinate complexes. Five-co-ordination is also present in the nickel chloride complexes whereas the corresponding bromide and iodide complexes are square-planar.

COMPLEXES of cyclic diamines have been extensively studied in recent years.[1-5] Very often such complexes exist in uncommon geometries due to the steric hindrance of the cyclic ligands.[6] Although 1,5-benzodiazepines have found extensive application in the pharmaceutical industry [7] and in some cases have carcinostatic activity,[8] relatively little work has been published on their behaviour towards metal ions. Recently some 2,4-dimethyl-1*H*-1,5-benzodiazepinium metal salts have been described.[9,10] We now report the preparation and characterisation of the nickel(II) and copper(II) complexes of a series of 2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepines, (I). In order to reduce the number of possible structures for the metal complexes we have only considered those ligands which exist in fixed-chair conformations at room-temperature.[11,12]



(I)

R^1 = Me,[2] R = R^3 = H, abbreviation used in this paper: meaz;
R^1 = R^3 = Me, R^2 = H, dmaz;
R^1 = R^3 = R^3 = Me, tmaz.

EXPERIMENTAL

Preparation of Compounds.—The preparation and characterisation of the ligands are described elsewhere.[11] All preparations of metal complexes were performed in anhydrous conditions using 2,2-dimethoxypropane as the dehydrating agent. The metal perchlorate hexahydrate or metal halide hydrate was shaken with 2,2-dimethoxypropane (*ca.* 5 ml/g metal salt) for an hour or more and left overnight. The solution, or suspension, was diluted with an equal quantity of dry ethanol and after standing for a short time was filtered. The filtrate was added dropwise with vigorous stirring to a dry ethanolic solution of the diazepine. Stirring was continued until precipitation occurred. In some cases diethyl ether was added to

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[2] H. D. Stevens and J. T. Yoke, *Inorg. Chim. Acta*, 1970, **4**, 244.

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[6] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

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[12] P. W. W. Hunter, Ph.D. Thesis, University of Surrey, 1972.

promote precipitation. In the case of the lightly substituted diazepines an excess of ether tended to produce an oil and oils may also result if the reactants are mixed too rapidly. The precipitates were filtered, washed with dry ethanol and ether, and then dried *in vacuo* over P_2O_5.

The preparation of the metal complexes is easiest with the more extensively methylated ligands and it is evident that the complexes are protected from solvent action by the methyl substituents.

Physical Measurements.—The electronic spectra were obtained by diffuse reflectance using a Unicam SP 700 with LiF as the reference sample.

The magnetic susceptibility data were determined by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. The room temperature measurements were made at *ca.* 3000 and *ca.* 5000 G. The low temperature measurements were made at *ca.* 3750, *ca.* 5750, and *ca.* 6700 G.

The vibrational spectra were recorded on a Perkin-Elmer 457 grating spectrometer. KBr plates were used in the region 4000—400 cm^{-1} and polythene plates in the region 500—250 cm^{-1}. The sample were prepared as Nujol or hexachlorobutadiene mulls.

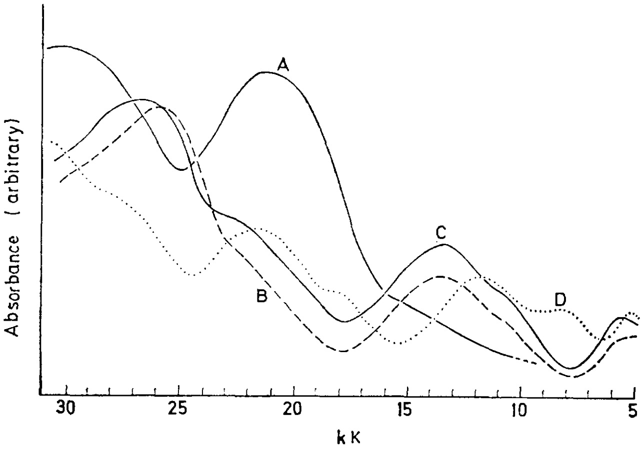


FIGURE 1 Solid reflectance electronic spectra of the nickel(II) complexes in the region 5—30 kK; A, $[Ni(meaz)_2](ClO_4)_2$; B, $[Ni(dmaz)_2Cl_2]$; C, $[Ni(meaz)_2Cl_2]$; D, $[Ni(tmaz)Cl_2]$

Microanalyses for C, H, N, and halogen were performed partly at the microanalytical laboratory of the University of Surrey and partly at the Bernhardt microanalytical laboratory (Table).

Analytical and magnetic data of some metal complexes of tetrahydro-1,5-benzodiazepines

				Elemental analysis (%)					
					Found			Required	
Complex	Colour	M.Pt. (°C)	μ(B.M.)[a]	C	H	N	C	H	N
$[Ni(meaz)_2](ClO_4)_2$	Orange	260	*d*	41·05	4·7	9·7	41·25	4·85	9·65
$[Cu(meaz)_2(CH_3OH)](ClO_4)_2$	Grey-green	204	1·78	41·3	5·05	9·25	40·75	5·2	9·05
$[Ni(meaz)_2Cl]Cl$	Pale green	211	3·23	52·7	6·3	12·25	52·9	6·2	12·35
$[Cu(meaz)Cl_2]$	Brown-green	135	1·74	41·75	3·75	9·55	40·5	4·75	9·45
$[Ni(dmaz)_2](ClO_4)_2$	Yellow-pink	268	d	43·8	5·75	8·8	43·3	5·3	9·2
$[Cu(dmaz)_2(CH_3OH)](ClO_4)_2$	Grey-green	202	1·92	42·85	5·75	8·6	42·4	5·6	8·65
$[Ni(dmaz)_2Cl]Cl$	Pale green	248	3·20	53·25	6·6	11·3	54·8	6·7	11·6
$[Cu(dmaz)Cl_2]$	Green	124	1·91	41·95	5·2	8·65	42·5	5·2	9·0
$[Ni(tmaz)_2](ClO_4)_2$	Orange-pink	269	d	45·35	5·7	8·85	45·15	5·7	8·8
$[Cu(tmaz)_2](ClO_4)_2$	Red-brown	203	1·84	44·6	5·5	8·85	44·85	5·65	8·7
$[Ni(tmaz)Cl_2]$	Light yellow	249	3·10	45·5	6·0	9·05	45·05	5·65	8·75
$[Ni(tmaz)_2]Br_2$	Orange	286	d	48·0	6·4	8·85	48·1	6·05	9·35
$[Ni(tmaz)_2]I_2$	Orange	251	d	41·55	5·35	8·1	41·6	5·25	8·1
$[Cu(tmaz)Cl_2]$	Green-brown	124	1·74	44·65	5·6	8·7	44·4	5·6	8·65

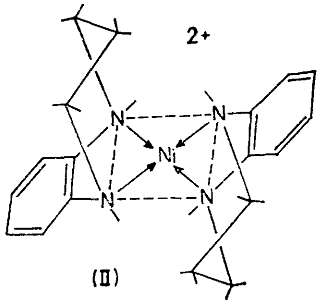
[a] The values of μ were recorded at 295 K, d = diagmagnetic.

RESULTS AND DISCUSSION

Nickel(II) *Complexes.*—The three nickel(II) perchlorate complexes are orange-yellow, diamagnetic solids indicating that they are square-planar species. Their electronic spectra are all similar to that of $[Ni(meaz)_2](ClO_4)_2$ shown in Figure 1.

The strong band at 21·3 kK and the broad band at 29—30 kK are typical of square-planar nickel(II) perchlorate complexes.[13] Since the chosen ligands are exceedingly unlikely to invert from the chair to the corresponding boat conformation, the *trans*-structure (II) is the most probable one for these complexes. In the alternative *cis*-structure 3H(axial)—3H′(axial) interaction between the two ligand molecules is severe.

The vibrational spectra of the nickel perchlorate complexes are very similar to those of the free ligands. In general the N–H stretching vibration at *ca.* 3200 cm^{-1} is lowered by *ca.* 150 cm^{-1} indicating nitrogen co-ordination. No significant splitting of the perchlorate bands in the 1110 and 620 cm^{-1} regions is observed, consistent with the absence of perchlorate co-ordination. Medium intensity bands *ca.* 283 cm^{-1} could be due to a Ni–N stretching vibration.



(II)

The electronic spectra of the nickel(II) halide complexes show that three different species are involved. The nickel(II) bromide and iodide complexes of tmaz are diamagnetic and their spectra indicate that they are similar to the corresponding perchlorate complexes.

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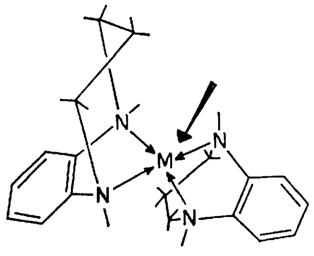
Their vibrational spectra are also similar to that of the corresponding perchlorate complex showing broad NH absorption *ca.* 3040 cm^{-1}.

The nickel(II) chloride complexes are paramagnetic with magnetic moments slightly above the spin-only value for two unpaired electrons. There are however two different stoicheiometries for the chloride complexes, NiL_2Cl_2 for meaz and dmaz and $NiLCl_2$ for tmaz. The smaller chloride ion appears to reside closer to the nickel(II) ion than do the bromide, iodide, or perchlorate ions, resulting in a less symmetrical electric field at the metal and a distortion from square-planar geometry. It is not always obvious from the electronic spectral and magnetic data when such a distorted complex can be considered as square-planar. For example, *X*-ray diffraction data have shown that some diamagnetic nickel(II) complexes of N_4 macrocycles are five-co-ordinate rather than square-planar in the solid state.[6,14]

It is difficult to reconcile the electronic spectra of the two NiL_2Cl_2 complexes with a six-co-ordinated tetragonal stereochemistry. If the bands at 26·5 and 13·7 kK are assigned to the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transitions (O_h notation), then the ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ transition should appear at about 8 kK. However the position of this transition is very susceptible to tetragonal distortions and is often split into two components, ${}^3B_{1g} \longrightarrow {}^3E_g, {}^3B_{2g}$ (D_{4h} notation). One of these components usually occurs *ca.* 8 kK and the other between 10 and 15 kK for distorted nickel(II) N_4 structures.[15,16] If the band observed *ca.* 5·7 kK is assumed to be a *d–d* transition and not totally due to vibrational overtones then it could be one of the components. The second component could be responsible for the weak shoulder observed *ca.* 11 kK. However this represents a larger splitting than is normally observed with bands at frequencies lower than usual.[16] The band at 13·7 kK is also lower in energy than is generally observed in the spectra of nickel(II) amine complexes.[15] The low energy of this band, the absence of a definite assignment to the ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ transition or its components, the pronounced shoulder *ca.* 23 kK and the relatively high intensity of the observed transitions indicate five-co-ordination. This could arise through axial co-ordination of one of the two chloride ions to give a square-pyramidal structure of C_{4v} symmetry.

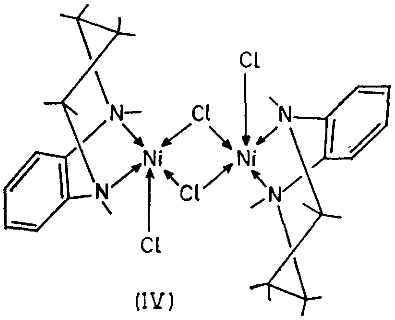
Further support for this structure could be forthcoming from conductivity data. However the complexes appear to be insufficiently soluble in suitable solvents and accurate data are not available.

Under C_{4v} symmetry the *d–d* transitions of the NiL_2Cl_2 complexes may be assigned as ${}^3B_1 \longrightarrow {}^3E$ *ca.* 5·8 kK; ${}^3B_1 \longrightarrow {}^3A_2, {}^3B_2$ *ca.* 11 kK; ${}^3B_1 \longrightarrow {}^3E$ *ca.* 13·7 kK; ${}^3B_1 \longrightarrow {}^3A_2(P)$ *ca.* 23 kK; and ${}^3B_1 \longrightarrow {}^3E(P)$ *ca.* 27·2 kK. These assignments are similar to those reported[6] for the five-co-ordinate complex [Ni(*NN'*-bis-(3-aminopropyl)piperazine)Cl]Cl. In order to permit the approach of a fifth donor atom a twisting of one of the two diazepine ligands away from the square-planar geometry is probable [structure (III)].



(III)

A similar axial approach is prevented in the complex of tmaz by the increased methyl-substitution of the ligand. The electronic spectrum of $Ni(tmaz)Cl_2$ closely resembles that of [Ni(bis(2-dimethylaminoethyl)methylamine)Cl_2] which is reported to be five-co-ordinate.[17] A similar five-co-ordinate structure may be achieved through chloro-bridging to give a dimeric structure [structure (IV)].



(IV)

The NH stretching vibrations of the nickel chloride complexes of meaz and dmaz appear *ca.* 3140 and 3150 cm^{-1} respectively. Strong bands at 311 and 305 and weaker bands at 260 and 263 cm^{-1} respectively could be due to Ni–N and Ni–Cl stretching vibrations. The vibrational spectrum of the nickel chloride complex of tmaz is dissimilar from the spectra of the other nickel chloride complexes and illustrates the change in structure.

Copper(II) *Complexes*.—The electronic spectra of some of the copper(II) complexes are reported in Figure 2. The *d–d* transition for the complex $[Cu(tmaz)_2](ClO_4)_2$ appears as a shoulder at 20—21 kK on a charge transfer band. Its position is similar to that reported for some CuN_4 square-planar complexes.[1] The frequency of the band is a little higher than is normally expected for copper(II) in this environment. The difference may be attributed to the very effective shielding of the axial co-ordination sites by the heterocyclic rings of the ligands.[18,19] The spectra of the copper perchlorate

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[18] W. K. Musker and M. S. Hussain, *Inorg. Chem.*, 1966, **5**, 1416.

[19] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, 1969, **5**, 47.

complexes of meaz and dmaz both exhibit a *d–d* transition *ca.* 17 kK. This is a much lower energy than is usually observed in square-planar CuN_4 complexes and is indicative of axial interaction giving rise to five- or six-co-ordination. The *d–d* transitions for copper(II) complexes with approximately trigonal-bypyramidal microsymmetry usually occur in the region *ca.* 10—15 kK [17,20–22] whereas for square-pyramidal complexes the region is *ca.* 16—19 kK.[1]

As in the case of the nickel halide complexes the decrease in methyl substitution in the ligands meaz and dmaz compared with tmaz may permit a donor atom to approach in an axial direction (Structure III). In the copper perchlorate complexes of meaz and dmaz the fifth donor atom is probably an oxygen atom of a co-ordinated methanol molecule. Their vibrational spectra show a broad absorption *ca.* 3500 cm^{-1} which is attributed to the OH stretching of the methanol.

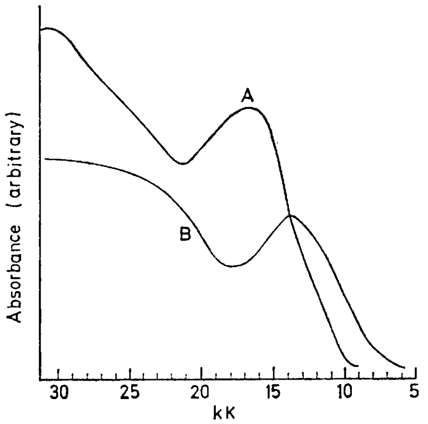

FIGURE 2 Solid reflectance electronic spectra of the copper(II) complexes in the region 5—30 kK; A, $[Cu(dmaz)_2(MeOH)](ClO_4)_2$; B, $[Cu(dmaz)Cl_2]$

In most regions the vibrational spectra of the copper and nickel perchlorate complexes of tmaz are superimposable, indicating a similar square-planar structure (II) for both. It is of some interest to compare the NH stretching frequency in the various perchlorate complexes with respect to the free ligands, since this could provide a measure of the co-ordination strength of the diazepine molecules, $\Delta\nu(NH) = \nu(NH)$ ligand — $\nu(NH)$ complex. In the three nickel perchlorate complexes the average value of $\Delta\nu(NH) = 137 \pm 12$ cm^{-1} and in the square planar copper perchlorate complex of tmaz $\Delta\nu(NH) = 135$ cm^{-1}. However, in the remaining two copper perchlorate complexes $\Delta\nu(NH) = 75$ cm^{-1} for meaz and 85 cm^{-1} for dmaz. This may be taken to indicate a weakening in the in-plane ligand-field strength, consistent with the axial approach of a fifth ligand in the formation of a five-co-ordinate complex. There is a concomitant decrease in the energy of the band attributed to a Cu–N vibration from *ca.* 310 cm^{-1} in the tmaz complex to 299 and 297 cm^{-1} in the meaz and dmaz complexes. However no firm conclusions should be based on these observations.

Copper(II) chloride readily produces complexes of stoicheiometry $CuLCl_2$ with each of the ligands meaz, dmaz, and tmaz. Although the *d–d* transition of the $Cu(meaz)Cl_2$ complex is obscured by a charge-transfer band, the other two complexes with tmaz and dmaz exhibit broad *d–d* bands centred at 13·6 and 14·0 kK respectively. The spectra are similar for example to those of some copper(II) bromide complexes of *NN'*-poly-substituted ethylenediamines, $CuLBr_2$, which have been assigned tetragonal structures achieved through halide-bridging.[23] Subsequent studies have shown however that these complexes are monomeric in solution and probably have distorted tetrahedral structures.[24]

Halide-bridged copper(II) complexes often exhibit magnetically concentrated behaviour. The room-temperature magnetic moments listed in the Table are a little lower than normal for copper(II) complexes although the susceptibilities are field independent at 300 K. Further, the variation of the magnetic moment of $Cu(tmaz)Cl_2$ with temperature shows no indication of magnetic exchange down to *ca.* 90 K. However, polynuclear halide-bridged copper(II) complexes are known which do not exhibit antiferromagnetic behaviour at temperatures between 300 and 90 K.[19] The magnetic moment of $Cu(tmaz)Cl_2$ decreases from 1·74 B.M. at 295·1 K to 1·69 B.M. at 89·4 K following a Curie–Weiss law with $\theta = 7°$.

The complexes exhibit two strong bands in the low frequency region of their vibrational spectra, at *ca.* 310 and *ca.* 250—270 cm^{-1} which may be assigned to Cu–N and Cu–Cl stretching vibrations. The NH stretching vibrations at *ca.* 3300 cm^{-1} in the free ligands are again lowered by *ca.* 110 cm^{-1} when the diazepine molecules are complexed.

Due to solubility problems accurate conductivity data is not available and it is not possible to make an unambiguous decision concerning the structure of the copper chloride diazepine complexes. However it is pertinent to note here that the reaction of cobalt chloride with tmaz yields a sky-blue compound of stoicheiometry $CoLCl_2$ and magnetic moment 4·86 B.M. The electronic spectrum of this compound exhibits multiple bands *ca.* 5·4 and *ca.* 15·1 kK characteristic of the tetrachlorocobaltate anion.[12] This illustrates that the steric requirements of the diazepine molecule discourage the formation of monomeric pseudotetrahedral species. The behaviour exhibited by the nickel halides described above tends to confirm this. It is suggested therefore that the copper(II) chloride diazepine complexes have a polymeric structure.

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