159. *Infrared and Nuclear Magnetic Resonance Spectra of Metal–Ethylenediamine Complexes.*

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Metal–ethylenediamine * complexes may be divided into two types on the basis of their infrared spectra. It is suggested that these correspond to *gauche* and *cis* configurations of the co-ordinated ethylenediamine molecules. An attempt to confirm the configuration difference by nuclear magnetic resonance spectroscopy was unsuccessful, probably because of mobility of the ring in the *gauche* form.

Infrared Spectra.—Following on previous studies of metal–ammonia complexes [1] it was thought that a spectroscopic investigation of a wide range of ethylenediamine complexes might give interesting comparisons, since the stability of these chelate complexes is generally greater than that of simple ammines and a larger range of metal ions can be investigated.

The infrared spectra of some metal–ethylenediamine complexes have been studied previously, notably the trisethylenediaminecobaltic complex [2] and many *cis–trans* isomers of cobalt(III) and chromium(III) of the type $[Co(en)_2X_2]$,[3] but the variation of the spectra with different metal ions has not been examined in detail. Accordingly we examined the spectra of a number of such complexes from 4000 cm.$^{-1}$ to 400 cm.$^{-1}$; the observed absorption frequencies are listed, weak bands being shown in *italics*, alongside Fig. 1, which shows

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* Throughout this paper the symbol (en) is taken to represent a co-ordinated ethylenediamine molecule.

[1] Powell and Sheppard, *J.*, 1956, 3108.

[2] Mizushima and Quagliano, (*a*) *J. Amer. Chem. Soc.*, 1953, **75**, 6084; (*b*) *J. Chem. Phys.*, 1954, **22**, 1614; (*c*) *J. Phys. Chem.*, 1955, **59**, 293.

[3] Merritt and Wiberley, *J. Phys. Chem.*, 1955, **59**, 55,

the spectra. The compounds were all obtained by standard methods. The octahedral complexes, prepared as hydrates, were heated to 120° to attempt to remove the water of crystallisation; only in the case of the nickel compound was this successful. Many of the complexes have spectra which in overall appearance are similar to that of $[Co(en)_3]^{3+}$, which we term type A spectra, whereas others give a rather simpler pattern of bands (type B spectra). It is clear that the absorption-band patterns of the two types of spectrum differ mainly in three regions, 1400—1250 cm.$^{-1}$, 1200—1000 cm.$^{-1}$, and 650—400 cm.$^{-1}$. The differences are shown most clearly in the octahedral complexes, where the absorption-band patterns for all the compounds having type A spectra are very similar, both in intensities and frequencies, whereas the type B pattern observed for trisethylenediaminenickel(II) shows marked differences in each of these regions. In particular, in the second region an outstandingly strong band is found for type B spectra at ~1030 cm.$^{-1}$, whereas type A spectra have several absorption bands of comparable intensity. The spectra from 650 cm.$^{-1}$ to 400 cm.$^{-1}$ are sometimes difficult to compare as the presence of water of crystallisation produces a strong broad band in this region.

Discussion of Infrared Spectra.—The very considerable differences between the type A and type B spectra are such as to make it improbable that they are caused by the effect of intermolecular forces between the complex ions. It seems that they must be related to the structure of the complex ions themselves.

Differences of this degree might occur between the spectra of complexes with different overall geometry, for example between octahedral and planar complexes, for such structural changes will cause different amounts of coupling between the vibrations of ligands attached to the same metal ion. However this cannot be the cause of the differences between the two types of spectrum as they are both observed for complexes with similar geometrical arrangements. Thus the octahedral complexes of Co^{III}, Cr^{III}, and Rh^{III} have type A spectra, but that of Ni^{II} is of type B; the planar complexes of Pt^{II} and Pd^{II} {and *trans*-$[Co(en)_2Cl_2]^+$} have type A spectra, whereas the spectrum of the planar $[Cu(en)_2]^{2+}$ ion is of type B. There are however more detailed differences between type A (or type B) spectra of octahedral and planar complexes, undoubtedly due to the different coupling between three and two co-ordinated ethylenediamine molecules respectively.

The only other likely cause of such pronounced spectral differences seems to be a change in configuration of individual co-ordinated ethylenediamine molecules. The likely configurations for such a chelate molecule are *cis* or *gauche* arrangements of the carbon and nitrogen skeleton. Until recently it was generally assumed that such ligands had the *cis* configuration, but definitive *X*-ray diffraction evidence has shown that $[Co(en)_3]Cl_3$ [4] and *trans*-$[Co(en)_2Cl_2]Cl$ [5] are in fact *gauche*. The infrared spectrum of $[Co(en)_3]Cl_3$ supports this conclusion.[2] On this basis the type A spectra, of which that of $[Co(en)_3]Cl_3$ is an example, correspond to *gauche* configuration of the ligand, whereas the type B spectrum may be assumed to correspond to the *cis* form. The higher local symmetry of the latter would account for the simpler spectra.

Although there seems no reasonable alternative explanation of the differences between the two classes of spectrum, an early reference [6] (of which we have only been able to obtain an abstract) refers to the conclusion from *X*-ray studies that in the $[Ni(en)_3]^{2+}$ ion the carbon and nitrogen atoms do not lie in the same plane, and this is one of the complexes which gives a type B spectrum. Our original measurements were made on the chloride, and the *X*-ray work was done on the nitrate, but we have since confirmed that the nitrate has a similar spectrum. There is here a conflict of evidence, which could best be resolved by a detailed *X*-ray diffraction study either of this compound, or of another one of those listed which has a type B spectrum.

[4] (*a*) Nakatsu, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1956, **29**, 428; (*b*) Saito, Nakatsu, Shiro, and Kuroya, *Acta Cryst.*, 1955, **8**, 729; (*c*) Nakatsu, Shiro, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158.

[5] Nakahara, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1952, **25**, 331.

[6] Watanabe and Atoji, *Science* (*Japan*), 1951, **21**, 301; *Chem. Abs.*, 1951, **45**, 9982 f.

We intend to publish later a detailed assignment of the spectra to the fundamental vibration frequencies of the complexes.

Nuclear Magnetic Resonance Spectra.—It was considered that the high resolution nuclear magnetic resonance spectra [7] of the complexes with type A and type B infrared spectra might also throw some light on the configurations of the co-ordinated ethylenediamine molecules. A number of those complexes studied by infrared means could not be investigated in this manner, because of either (*a*) limited solubility in water (solid samples do not give high resolution spectra), or (*b*) paramagnetism of the complex (this causes a broadening and merging together of the resonance absorption bands at reasonable concentrations in the solution). However, nuclear magnetic resonance spectra were obtained of $[Co(en)_3]Cl_3$, $[Rh(en)_3]Cl_3$, $[Pt(en)_2]Cl_2$, $[Pd(en)_2]Cl_2$, and $[Zn(en)_2]C_2O_4$. Of these complexes the zinc compound gave a very sharp resonance line from the hydrogen atoms of the CH_2 groups, whereas rhodium, palladium, and platinum complexes as a group gave resonance bands of similar shape which were, however, of considerable breadth and had indications of unresolved fine structure (Fig. 2). The latter feature might have been caused by either (*a*) electron-coupled spin–spin interaction between two pairs of non-equivalent hydrogen atoms as might occur with a rigid *gauche* form of the ligand, but not with the *cis* form, (*b*) similar spin–spin interaction between CH_2 and NH_2 groups if the hydrogen atoms of the latter do not exchange sufficiently rapidly with those of the water solvent, or (*c*) a combination of these two effects.

FIG. 1. *Infrared spectra of metal–ethylenediamine complexes in the region* 1750—400 *cm.*$^{-1}$ (*Hilger* H800 *spectrometer with* NaCl *and* KBr *prisms*). *The two types of spectrum are designated by* A *and* B. *Broken portions of the curves correspond to hexachlorobutadiene mulls, others to Nujol mulls.*

$[Co(en)_3]Cl_3$ (octahedral hydrate): 3510—3440; 3195—3060; 1619; 1591—1563; 1466; 1366; 1325; *1302*; *1277*; 1251; *1218*; 1163—1155; 1122; 1057; *1002*; *894*; 782; *744*; 523—490—465—435 (Type A).

$[Cr(en)_3]Cl_3$ (octahedral hydrate): 3360; 3190—3060; *2945—2891*; 1620; 1574—1544; 1463; *1394*; 1359; 1330; 1303; *1275*; 1225; 1153—1144; *1115*; 1053; *1005*; *880—869*; 738; 555—530—480—445 (Type A).

$[Rh(en)_3]Cl_3$ (octahedral hydrate): 3528—3440; 3222—3095; 2697—2773; 1620; 1570; 1460; 1364; 1327; 1306; 1279; 1239; 1215; 1165—1156; 1124; 1057; 879; 793; 751; 723; 578—530—506—465 (Type A).

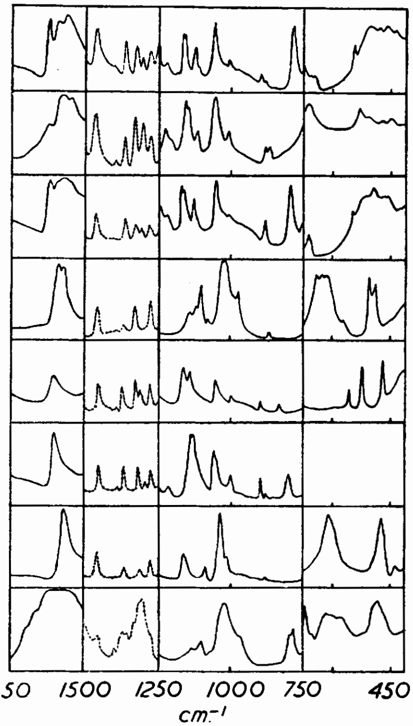
$[Ni(en)_3]Cl_2$ (octahedral): 3480—3400; 3250; 2940—2875; 1587—1569; 1457; *1393*; *1369*; 1330; 1275; 1140—1118—1100; *1072*; 1026—974; *865*; 705—683—662; 522—498 (Type B).

$[Pt(en)_2]Cl_2$ (planar): 3207—3141—3064; 1610; 1454; 1373; 1326; 1311; 1275; 1154—1138; 1050; 999; 897; *876*; 831; 589; 546; 478 (Type A).

$[Pd(en)_2]Cl_2$ (planar): 3190—3145—3046; 2960—2875; 1601; 1452; *1390*; 1367; 1317; *1293*; 1273; *1210*; 1134—1125; 1055; *997*; 894; *875*; 798. (Not examined in potassium bromide region) (Type A).

$[Cu(en)_2][PtCl_4]$ (planar): 3562; 3300—3230; 2940—2878; *1633*; 1587; 1459; *1365*; *1315*; 1277; 1162; 1089; 1040—1015; *975*; 700; 550 (Type B).

$[Zn(en)_2][C_2O_4]$ (tetrahedral): *3505—3425*; 3291—3159; *2914—2869*; near 1600 broad band; *1455*; *1398*; 1371; 1303; *1130*; *1100*; 1021; 794—783; 743; 680—625; 500 (spectrum is complicated by presence of strong oxalate bands, but appears to be of type B).



The presence of effect (*b*) can be readily checked by dissolving the substance in D_2O and thereby replacing the hydrogen atoms of the NH_2 groups by deuterium. Because of

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[7] Wertz, *Chem. Rev.*, 1955, **55**, 829.

the different magnetic moment and spin of the latter nucleus any interaction of the ND_2 groups with the CH_2 hydrogen atoms is expected to be much smaller. In fact in all cases except the cobalt complex, replacement of the NH_2 groups by ND_2 caused the broad resonances to become sharp lines as in the case of the zinc compound, showing that effect (*b*) was the only operative one. With the cobaltic complex a rather broader resonance band was originally observed for the CH_2 groups, presumably owing to the presence of extra structure caused by interaction with the magnetic moment of the cobalt nucleus of spin $\frac{7}{2}$; as expected some line-breadth persisted in the spectrum of the deutero-compound.

The fact that each of the CH_2 resonances consists of a sharp line after elimination of the effect due to NH_2 hydrogen atoms shows that all the four methylene hydrogen atoms are effectively chemically equivalent. This would be expected for the *cis* configuration of the co-ordinated ethylenediamine molecule which has a plane of symmetry through the two carbon and two nitrogen atoms. In the case of a fixed *gauche* configuration, the plane of symmetry is destroyed and the two-fold axis through the centre of the carbon–carbon bond causes the hydrogen atoms to be structurally equivalent only in two separate pairs. However, if the co-ordinated molecule can change with sufficient rapidity from one *gauche* form to the equivalent form obtained by movement of the carbon and nitrogen atoms through the median plane, then the plane of symmetry is effectively restored. As a likely chemical shift between the two non-equivalent pairs of hydrogen atoms of the *gauche* form is about 10 c./sec., the simplified spectra will be observed if the *gauche* forms are being interconverted with about this order of magnitude of frequency. This is probably why the nuclear magnetic resonance spectra do not allow a distinction to be made between the configurations suggested by infrared means.

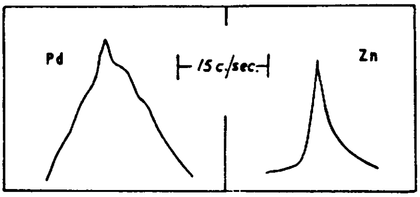

FIG. 2. *Nuclear magnetic resonance spectra of the hydrogen nuclei of* CH_2 *groups in the ethylenediamine complexes* $[Pd(en)_2]Cl_2$ *and* $[Zn(en)_2]C_2O_4$ *scanned at the same rate (Varian Associates* 4300 B *spectrometer); the spectra are slightly asymmetrical owing to inclusion of a small amount of dispersion with the absorption mode.*

Conclusion.—The infrared spectra provide a criterion for dividing the metal–ethylenediamine complexes into two types, and it is suggested that these correspond to the alternative *gauche* and *cis* configurations of the ligand. Attempts to confirm these structural conclusions by nuclear magnetic resonance spectra were unsuccessful, probably owing to the mobility of the ring in the *gauche* configuration.

It is noteworthy that, of the complexes studied, those with type A spectra, *i.e.*, with *gauche* configurations, are more stable than those with type B spectra, although as yet too few have been investigated to make a reliable generalisation on this point. Also, we noted during the nuclear magnetic resonance experiments that the hydrogen atoms of NH_2 groups of co-ordinated ethylenediamine molecules exchange with deuterium in D_2O solutions at very different rates. Thus, with $[Pt(en)_2]Cl_2$ the exchange took about 12 hr. to go to completion, whereas with $[Rh(en)_3]Cl_3$ the exchange took about 30 min. The lack of observation of structure on the CH_2 resonances of $[Zn(en)_2]C_2O_4$ implies that in this case the NH_2 hydrogen atoms of the ligand exchange at a rate probably exceeding 100 sec.$^{-1}$, *i.e.*, $2\pi\Delta\nu$, where $\Delta\nu$ ($\sim$15 c./sec.) is a typical half-width of a band with structure due to spin–spin coupling of CH_2 and NH_2 groups (see Fig. 2).

Another interesting difference between the spectra of the platinum and rhodium complexes is that whereas the ^{195}Pt nucleus (spin $\frac{1}{2}$, natural abundance 34%) causes an extra pair of bands in the spectrum of the CH_2 group centred about the main resonance with the surprisingly large spin–spin splitting of $\sim$45 c./sec., the abundant ^{103}Rh nucleus (also with spin $\frac{1}{2}$) does not appear to cause an observable splitting of the CH_2 resonance. Under the experimental conditions such a splitting must be less than 3 c./sec. Thus the Pt–H coupling constant is at least 15 times greater than the corresponding Rh–H constant, although the magnetogyric ratio of the ^{195}Pt nucleus is only 6 times that of ^{103}Rh. This implies that the intervening electron distributions couple together the platinum and hydrogen nuclei more effectively than rhodium and hydrogen.

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