

224. Infrared Spectra and the Stabilities of Chelate Metal-Ethylenediamine Complexes.

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Infrared absorption bands due to NH_2 rocking and metal-nitrogen stretching frequencies of metal-ethylenediamine co-ordination complexes are correlated with the stability of the complexes, irrespective of whether the spectra are of type A or type B. *X*-Ray evidence, published elsewhere, has shown that type B spectra do not correspond to a planar *cis*-configuration of the ligand.

It has been noted¹ that the infrared spectra of some chelate metal-ethylenediamine complexes fall into two classes, A and B, and that this classification can be made regardless of the overall symmetry of the complex (octahedral, square-planar, or tetrahedral). It was suggested, as a possible cause of the difference, that in compounds giving type A spectra the ligand adopts the *gauche* conformation, giving a non-planar 5-membered ring, whereas in those giving type B spectra the ligand has the *cis*-configuration, corresponding to a planar ring. However, it was pointed out that a preliminary *X*-ray study had given an indication that $[\text{Ni en}_3]^{2+}$ (*en* = ethylenediamine), which gave a type B spectrum, has a non-planar 5-membered ring;² we have since found that a more detailed *X*-ray study has been made³ of another ion with a type B spectrum, $[\text{Cu en}_2]^{2+}$, and this leaves no doubt that it has non-planar rings with near-*gauche* conformations. Our suggested explanation for the difference between type A and type B spectra must now be abandoned.

In a detailed investigation of some of the spectra we have also found their appearance to be affected in part by hydrogen-bonding between NH and the anion. This is particularly true of the spectra of the $[\text{Pt en}]_2^{2+}$ and $[\text{Pd en}_2]^{2+}$ ions: the point is considered in more

¹ Powell and Sheppard, *J.*, 1959, 791.

² Watanabe and Atoji, *Science (Japan)*, 1951, **21**, 301; *Chem. Abs.*, 1951, **45**, 9982.

³ Scouloudi, *Acta Cryst.*, 1953, **6**, 651.

detail in another paper.⁴ However, hydrogen-bonding effects can be minimised by choosing a large complex anion,⁵ so we now present spectral data for the tetrachloroplatinates(II) of a number of the ethylenediamine complexes. Without complications due to hydrogen bonding, it is now more apparent than previously that there is good correlation between certain features of the whole family of spectra, whether of type A or of type B, and the general stability of the complexes. These features of continuity occur despite the fact that we have still been able to classify all the spectra so far obtained as

Frequencies of δNH_2 rocking and $\nu\text{M-N}$ vibrations (cm^{-1}), and stabilities of metal-ethylenediamine complexes.

Metal	$\log k_{\text{average}}$	$\log K_1$	Spectrum type	δNH_2 rock		$\nu\text{M-N}$
Pt(II)	$\beta_2/2 = ?$?	A	795	780	583
Rh(III)	$\beta_3/3 = ?$?	A	783	773	580
Co(III)	$\beta_3/3 = 16.3^a$	18.7^b	A	782	770	585
Pd(II)	$\beta_2/2 = 13.5^c$?	A	765	750	573
Cr(III)	$\beta_3/3 = ?$?	A	726	708	567
Hg(II)	$\beta_2/2 = 11.7^d$	12.1^e	B	727	695	?
Cu(II)	$\beta_2/2 = 9.8^e$	10.55^e	B	705sh	694	538
Ni(II)	$\beta_3/3 = 6.0^e$	7.52^e	B	653	640sh	515
Co(II)	$\beta_3/3 = 4.6^a$	5.89^a	B	635	620sh	502
Zn(II)	$\beta_3/3 = 4.0^e$	5.71^e	B	620	598	478
Cd(II)	$\beta_3/3 = 4.0^e$	5.47^e	B	622	599	478

^a Bjerrum, "Metal-Amine Formation," P. Haase and Son, Copenhagen, 1941. ^b Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265. ^c Mellor and Maley, *Nature*, 1948, **161**, 436. ^d Bjerrum, *Chem. Rev.*, 1950, **46**, 381. ^e Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

type A or type B on grounds of the patterns of intensities of bands in the 1200—1000 cm^{-1} region. However, it now seems possible that spectra of intermediate type may be found later.

The spectra of a typical range of the complexes are shown in the Figure, in the general order of decreasing stability (a—h). The sequence from mercury(II) to zinc(II) is based on numerical stability constants.⁶ The figures given here have been based on results obtained, as far as possible, under comparable conditions of temperature and concentration. $\log k_{\text{average}}$ is taken as the logarithm of the overall stability constant ($\log \beta_n$) divided by the number (n) of groups bound to the metal ion in the usual complex. In some cases there is uncertainty as to how ethylenediamine groups are uniformly bound in the complex, and so, in addition, where available, the figures for the first successive stability constants are also given. For the more stable complexes, actual stability constants are only available for cobalt(III) and palladium(II). On general chemical grounds there is little doubt that the platinum(II) and rhodium(III) complexes are comparable in stability with cobalt(III), and that those of chromium(III) and palladium(II) are rather less stable, but the exact order is uncertain. The spectra from mercury(II) to zinc(II) are of type B, *i.e.* they show an outstandingly strong band near 1000 cm^{-1} . The others, of more stable complexes, are of type A.

The most interesting features of continuity which follow through the whole series of spectra, are a series of well-defined bands varying in position from about 800 cm^{-1} in the spectra of the most stable complexes to near 600 cm^{-1} in the spectrum of the least stable complex ion, $[\text{Zn en}_2]^{2+}$. These bands are caused principally by NH_2 rocking vibrations. Another sequence of bands, which may be assigned to metal-nitrogen bond stretching, also show regular frequency changes from about 585 to 478 cm^{-1} in the same series of complexes. These assignments are discussed in detail elsewhere.⁴

These bands are listed in detail in the Table for all the complexes examined, including

⁴ Powell and Sheppard, *Spectrochim. Acta*, in the press.

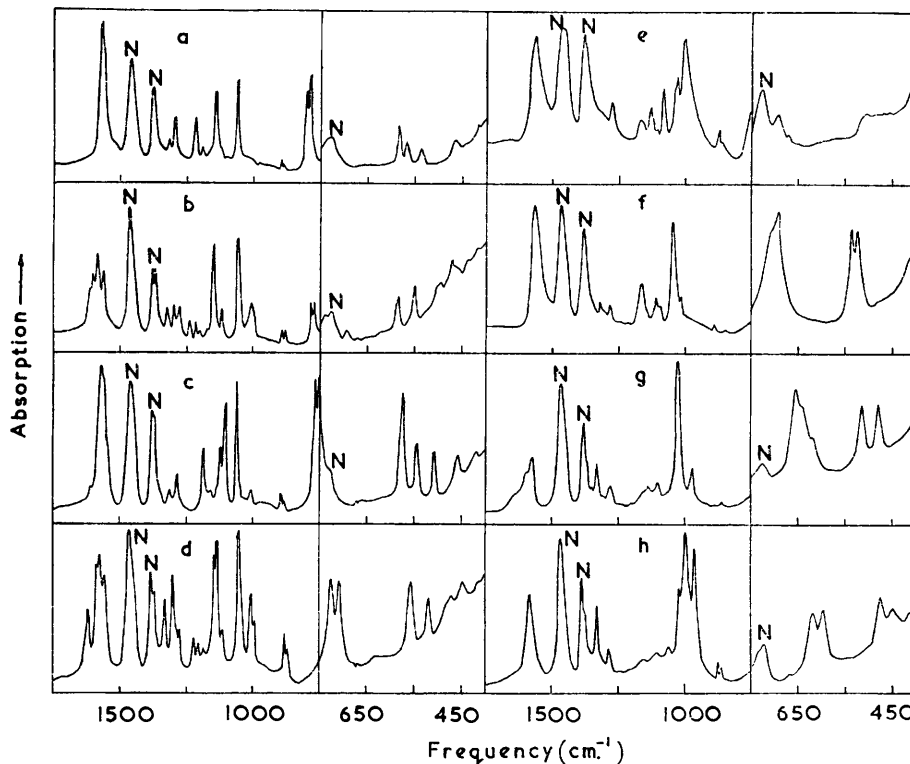
⁵ Ebsworth and Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.

⁶ Sutton *et al.*, "Stability Constants," *Chem. Soc. Spec. Publ. No. 13*, 1958.

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some not shown in the Figure. It may be seen that they are correlated successfully with stability data for the complexes, although it is understood that other factors than the strength of metal-nitrogen bonding must contribute to the stability of these ions in solution.

Infrared spectra of metal-ethylenediamine complexes as tetrachloroplatinates(II); range 1750—400 cm^{-1} ; Nujol dispersions (Nujol peaks marked N).



(a) Pt(II); (b) Co(III); (c) Pd(II); (d) Cr(III); (e) Hg(II); (f) Cu(II); (g) Ni(II); (h) Zn(II).

However in a study of the complex amines,⁷ similar regularities were found between the NH_3 deformation and metal-nitrogen stretching frequencies, and the general order of stability of the complexes.

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⁷ Powell and Sheppard, *J.*, 1956, 3108.