

INFRARED SPECTRA OF SOME BIS(8-AMINO-2-METHYLQUINOLINE)-METAL COMPLEXES. EVIDENCE FOR *CIS* CONFIGURATIONS

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Abstract

The infrared spectra of a number of bis- and mono-complexes of 8-amino-2-methylquinoline (maq) have been recorded and the possibility of a *cis* configuration of the two bidentate ligands in the bis-chelated complexes is discussed with respect to the complexity in the 850–700 cm^{-1} region.

INTRODUCTION

Although the small differences in the infrared spectra of geometrical isomers do not provide a general method for the distinction of *cis* and *trans* isomers,¹ several workers have suggested that splitting of in-phase, out-of-plane, C–H bending modes for bis-bipyridyl complexes^{2,3} and for bis-pyridine complexes⁴ can be used as a criterion for the presence of the *cis* isomer. McWhinnie⁵ has reported the absence of splitting of the in-phase, out-of-plane C–H deformation mode for bis-bipyridyl complexes of cobalt(II), nickel(II), and rhodium(II) considered to contain the two bipyridyl ligands in a *trans* configuration. We now report observations on some transition metal complexes of 8-amino-2-methylquinoline.

RESULTS AND DISCUSSION

The ligand 8-amino-2-methylquinoline (maq) shows C–H out-of-plane deformations at 831s, 796m, and 746s cm^{-1} . The spectrum in this region can be interpreted by considering separately the three adjacent ring hydrogen atoms (carbocyclic ring) and the two adjacent ring hydrogen atoms (heterocyclic ring).^{6a} The presence of two adjacent free hydrogen atoms should produce a strong band in the 860–800 cm^{-1} region.⁷ No strong bands should be present in the 750–700 cm^{-1} region although weak bands sometimes occur. The strong band at 831 cm^{-1} in the spectrum of maq

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¹ Wilkins, R. G., and Williams, M. J. G., in "Modern Coordination Chemistry." (Eds J. Lewis and R. G. Wilkins.) (Interscience: New York 1960.)

² Martin, B., McWhinnie, W. R., and Waind, G. M., *J. inorg. nucl. Chem.*, 1961, **23**, 207.

³ Beck, W., and Schnierer, E., *Chem. Ber.*, 1962, **95**, 3048.

⁴ Rao, G. S., *Z. anorg. Chem.*, 1960, **304**, 77.

⁵ McWhinnie, W. R., *J. inorg. nucl. Chem.*, 1964, **26**, 15.

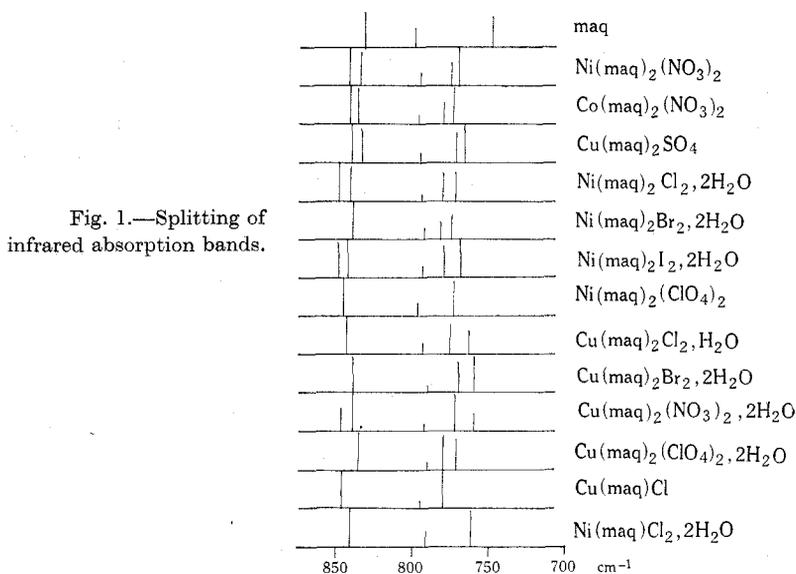
⁶ Bellamy, L. J., "The Infra-red Spectra of Complex Molecules." (a) p. 78; (b) p. 281. (John Wiley: New York 1964.)

⁷ Bomstein, J., *Analyt. Chem.*, 1953, **25**, 512.

can therefore be assigned to the out-of-plane C-H deformation of the two adjacent hydrogen atoms. The related compounds, 2,6- and 2,7-dimethylquinoline, which have only two adjacent free hydrogen atoms in each of the two rings, absorb strongly at 831 cm^{-1} and 835 cm^{-1} respectively.^{6b}

The band of medium intensity at 796 cm^{-1} is almost certainly associated with the presence of the three adjacent free hydrogens on the carbocyclic ring as aromatic rings with three adjacent hydrogen atoms show an absorption in the $810\text{--}750\text{ cm}^{-1}$ region.⁸ 8-Hydroxyquinoline, containing three adjacent hydrogen atoms in each ring, shows a strong band at 780 cm^{-1} . The strong band at 745 cm^{-1} in the spectrum of maq is also most likely due to C-H deformations of the three adjacent hydrogen atoms.

The data presented in Figure 1 show that, on coordination of maq, significant shifts occur for the out-of-plane C-H bending modes of the free ligand. The bands at 831 and 745 cm^{-1} are shifted to higher wave numbers, whilst the band at 796 cm^{-1} is shifted slightly to shorter wave numbers.



The complex $[\text{Ni}(\text{maq})_2(\text{NO}_3)](\text{NO}_3)$ ⁹ has been shown by a three-dimensional X-ray analysis to have a highly distorted octahedral configuration.¹⁰ The two ligand molecules are arranged *cis* to each other, the heterocyclic nitrogen atoms being *trans* as shown in Figure 2. Infrared evidence had previously suggested the presence of a bidentate nitrato group.⁹ The analogous cobalt(II) complex, $\text{Co}(\text{maq})_2(\text{NO}_3)_2$ also contains a bidentate nitrato group (i.r. bands at 1493s , 1280s , 805m , and 743m cm^{-1}) and is, therefore, most probably octahedral with a *cis* configuration of the two ligand molecules. Both of these complexes show complexity in the infrared in the region of interest.

⁸ Werner, R. L., Kennard, W., and Rayson, D., *Aust. J. Chem.*, 1955, **7**, 346.

⁹ Litzow, M. R., Power, L. F., and Tait, A. M., *J. chem. Soc. (A)*, 1970, 275.

¹⁰ Tait, A. M., Ph.D. Thesis, University of Queensland, 1970.

Models indicate that a *trans*-planar arrangement of the two maq molecules is impossible due to steric effects associated with the presence of the methyl groups in the 2-positions. One would expect that in all octahedral bis-maq complexes, the two ligand molecules would occupy similar positions about the metal as that found in $[\text{Ni}(\text{maq})_2(\text{NO}_3)]\text{NO}_3$. If the splitting observed in the 850–750 cm^{-1} region in the infrared for the nickel(II) and cobalt(II) nitrate complexes is diagnostic of the *cis* isomer of octahedral bis-maq complexes, it should be observed in all of the bis octahedral complexes of maq.

Figure 1 shows the results obtained for a series of complexes of nickel(II)⁹ and copper(II).¹¹ Some degree of splitting is observed in all of the bis octahedral complexes, with the exception of $\text{Ni}(\text{maq})_2(\text{ClO}_4)_2$ and in this respect complements the work of McWhinnie.⁵ This evidence for *cis* configuration may not be conclusive, since it is not possible to obtain the corresponding *trans* complexes in order to check if the splitting is absent. The mono-chelated complexes of nickel(II)⁹ and copper(II)¹¹ of type $\text{Ni}(\text{maq})\text{X}_2 \cdot x\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, x = 2, 7/2, 2$ respectively) and $\text{Cu}(\text{maq})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$) do not show splitting of the in-phase, out-of-plane C–H deformation modes of the ligand molecule.

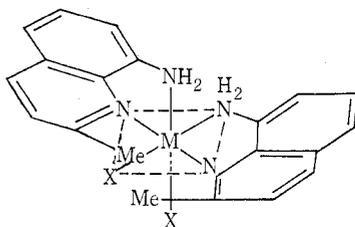


Fig. 2.—*cis* configuration for bis-maq complexes.

The complex $\text{Ni}(\text{maq})_2\text{I}_2 \cdot 2\text{H}_2\text{O}$ is thought to contain the tetrahedral anion $[\text{Ni}(\text{maq})_2]^{2+}$ in the solid.⁹ This compound also shows complexity in the region of interest, possibly indicating that splitting observed in the 850–750 cm^{-1} region of the spectrum is due to a non-planar arrangement of the two maq molecules. The disposition of the ligand molecules in a regular tetrahedral complex does not differ greatly from that in a *cis*-octahedral complex, so perhaps it is not surprising that splitting is observed in $[\text{Ni}(\text{maq})_2]\text{I}_2 \cdot 2\text{H}_2\text{O}$.

Several workers²⁻⁵ have attributed the greater complexity in the spectra of some complexes to the lower symmetry of the *cis*-isomer and Cotton¹² has pointed out that a surrounding crystal field of symmetry lower than that of the complex may resolve degenerate modes or cause normally infrared-inactive vibrations to become active. For these maq complexes the reason for the absence of splitting of the highest wave-number band for some of the complexes is unknown.

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer 337 grating infrared spectrophotometer. The complexes were prepared as Nujol mulls or ground with potassium bromide to form disks.

¹¹ Litzow, M. R., Power, L. F., and Tait, A. M., unpublished data.

¹² Cotton, F. A., in "Modern Coordination Chemistry." (Eds J. Lewis and R. G. Wilkins.) (Interscience: New York 1960.)