Neutral Transition-metal Complexes as Probes for Solvent Structure. The Spectrophotometric Properties of [*NN'*-1-Methylethylenebis(*o*-aminobenzylideneiminato)]cobalt(II) in some Pure and Mixed Solvents

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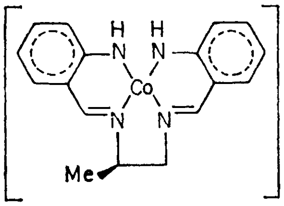
The visible spectrum of the rigid planar complex [*NN'*-1-methylethylenebis(*o*-aminobenzylideneiminato)]-cobalt(II), [Co(meab)], has been studied in a range of pure and mixed aqueous solvent systems under deoxygenated conditions. Beer's law is obeyed in each system up to the solubility limit. Although the visible spectrum of [Co(meab)] in water is essentially featureless, maxima at 421—435 and 522—531 nm develop on addition of methanol, ethanol, n-propanol, t-butyl alcohol, acetone, and pyridine. The close similarity of the visible spectra in pure pyridine and benzene solvents suggests that this effect is not due to discrete axial ligation of [Co(meab)] by solvent molecules, as confirmed by magnetic-moment measurements in aqueous pyridine and by the isolation of a solvate, rather than a pyridine-containing complex, from saturated solutions of [Co(meab)] in pyridine. The absorption coefficient of [Co(meab)] in binary aqueous mixtures appears to be related to the structure of the bulk solvent environment.

INVESTIGATION of the thermodynamic, structural, and other physical properties of water[1] and other solvent systems[2] has been an important area of research for many years. One approach in these studies has been to examine the solvent dependence of the spectral properties of solutes.[2] The formal neutrality, planar rigidity,[3] and notable lack of a tendency to axial ligation[3,4] of [*NN'*-1-methylethylenebis(*o*-aminobenzylideneiminato)]cobalt(II), [Co(meab)], commend its use as a probe for solvent structure because the interpretation of its visible spectral properties is not likely to be complicated by the effects of ion association and/or changes in co-ordination number or ligand geometry.



[Co(meab)]

In this paper we report the spectral properties of [Co(meab)] in water, methanol, ethanol, n-propanol, t-butyl alcohol, pyridine, benzene, and acetone, and in mixtures of these solvents (except benzene) with water. The [Co(meab)] centre seems to mirror changes in its general solvent environment rather than undergo discrete axial ligation.

EXPERIMENTAL

Materials.—The solvents used in this work were purified by established methods and their properties agreed closely with literature data. Solvents were generally stored in the dark over molecular sieves in a nitrogen atmosphere. The complex [Co(meab)] was prepared under nitrogen.[4] The solvates [Co(meab)]·py and [Co(meab)]·dmf were isolated by evaporation of saturated solutions of the complex in pyridine and *NN*-dimethylformamide.[4]

Procedure.—The appropriate solvent mixture was made up volumetrically under positive nitrogen pressure and thermostatted within ±0.1 °C of the desired temperature. After addition of a weighed amount of [Co(meab)], final volume adjustments were made by adding the more volatile component. Control experiments were made to minimize dilution effects due to volume changes at the various temperatures employed. A Beckman DK-1 spectrophotometer, fitted with a temperature-controlled cell housing, was used to obtain u.v.–visible spectra of the solutions in 10 and 100 mm matched quartz cells in the absence of oxygen. This precaution is necessary to avoid aerobic oxidation to a cobalt(III) meab derivative, which would otherwise precipitate from all the solvents investigated (see Figure 1). Repeated absorbance readings generally agreed to better than ±1.5%. Solution magnetic moments were obtained by the Evans method[5] from n.m.r. spectra of saturated solutions of [Co(meab)] recorded on a Varian T-60 spectrometer at 25 ± 1 °C. Solutions were scanned under a positive nitrogen pressure in precision coaxial n.m.r. tubes (Wilmad Glass Co., no. 517, I, II) using tetramethylsilane and $[Me_4N]Cl$ as internal references. The procedure was standardized using copper(II) sulphate in water ($\mu_{eff.}$ 1.95 B.M. at 25 °C).†

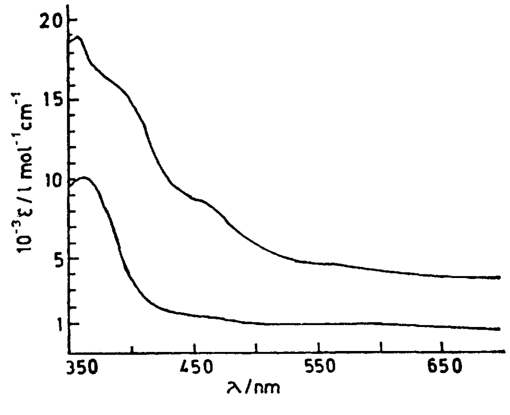


FIGURE 1 Visible spectrum of [Co(meab)] and its air-oxidized form (upper curve) in water at 25 °C. The spectra of [Co(meab)] are identical at pH 2 and 14

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† 1 B.M. ≈ 9.27×10^{-24} A m².

[1] 'Water: A Comprehensive Treatise,' ed. F. Franks, Plenum Press Inc., New York, 1972.

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[3] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 2531, 3105.

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RESULTS AND DISCUSSION

Spectral results for free meab and [Co(meab)] in a range of pure solvents are collected in the Table. These results support the stereochemical integrity of the square-planar complex[3,4] and its spectral sensitivity to the nature of the solvent.

Pure Solvent Spectra.—Although the wavelength maximum for the free ligand varied little with solvent in the series ethanol (342), pyridine (350), and water (350 nm), the absorption coefficient, ε, at 350 nm was solvent dependent, increasing by a factor of *ca*. 4 from water to ethanol. The introduction of Co^{II} into the ligand system caused an increase in ε at 350 nm in water and pyridine and a slight decrease in ethanol. At the same time the spectral maxima in this region shifted to longer wavelength by *ca*. 10, 28, and 25 nm in water, ethanol, and pyridine, respectively (Table). The results for [Co(meab)] in the 360—375 nm region are consistent with its general solvation rather than with specific hydrogen-bonding solvational interactions,[6] as supported by the observation of an absorption maximum at 373 nm in benzene which can neither form hydrogen bonds nor occupy an axial metal co-ordination site.

Spectral parameters for meab and [Co(meab)] in deoxygenated solvents at 25 °C

Solvent	$\lambda_{max.}$[a] ($10^{-4}\varepsilon$)[b]	$\lambda_{max.}$[a] ($10^{-4}\varepsilon$)[b]	$\lambda_{max.}$[a] ($10^{-4}\varepsilon$)[b]
(*a*) meab			
Water	350 (0.267, 0.885[c])		
Ethanol	342 (1.06, 0.940[c])		
Pyridine	350 (0.471, 0.947[c])		
(*b*) [Co(meab)]			
Water[d]	350 (0.885)		
Methanol	366 (1.11)	421 (1.11)	522 (0.285)
Ethanol	370 (1.26)	425 (1.62)	528 (0.393)
n-Propanol	370 (1.36)	426 (1.74)	525 (0.425)
t-Butyl alcohol	372 (1.79)	428 (2.42)	531 (0.817)
Acetone	373 (1.48)	428 (1.85)	528 (0.474)
Pyridine	375 (1.21)	434 (1.73)	531 (0.442)
Benzene	373 (1.44)	434 (1.71)	527 (0.508)

[a] Units are nm. [b] Units are $l\ mol^{-1}\ cm^{-1}$. [c] Values of ε for [Co(meab)]. [d] Aqueous solutions of [Co(meab)] have no discernible spectral maxima in the regions 421—434 and 522—531 nm (see Figure 1); the average values of ε in these wavelength ranges are *ca*. 0.18×10^4 and 0.12×10^4 $l\ mol^{-1}\ cm^{-1}$, respectively.

In anhydrous solvents [Co(meab)] exhibited spectral maxima in the 421—434 and 522—531 nm regions which were not observed in pure water (compare Figures 1 and 2). The ε values at these new maxima were typically 5—10 times greater than those in water. Beer's law was obeyed up to the solubility limit in all solvents. The wavelengths of maximum absorbance showed little variation with solvent while the corresponding ε values were solvent dependent. Of particular note is the close similarity of the spectra of [Co(meab)] in pyridine, acetone, and benzene. These observations confirm that [Co(meab)] has no significant tendency towards self association (adherence to Beer's law) or discrete axial ligation by solvent molecules (similarity of spectra).[3,4] The magnetic moment of [Co(meab)] in pyridine containing up to 50% v/v water was 2.07 ± 0.07 B.M. (four determinations) which is close to $\mu = 2.2$ B.M. reported in the solid state[4] and is characteristic of square-planar Co^{II}.[4,7] The ε values increased with the solubility of [Co(meab)], being greatest in pyridine, benzene, acetone, and t-butyl alcohol (solubility *ca*. 1×10^{-3} mol l^{-1}, *cf*. *ca*. 1×10^{-5} mol l^{-1} in water), and do not depend on the co-ordinative nature of the solvent (compare pyridine and benzene). It is clear that the marked spectral shifts which occur on addition of pyridine to solutions of [Co(salen)] [salen = *NN'*-ethylenebis(salicylideneiminato)],[8-10] [Co(meab)X_n],[4] and metalloporphyrins[11] in weakly co-ordinating solvents are due to increased co-ordination at the metal centre. This feature is absent in [Co(meab)], but the ε values are nevertheless solvent dependent.

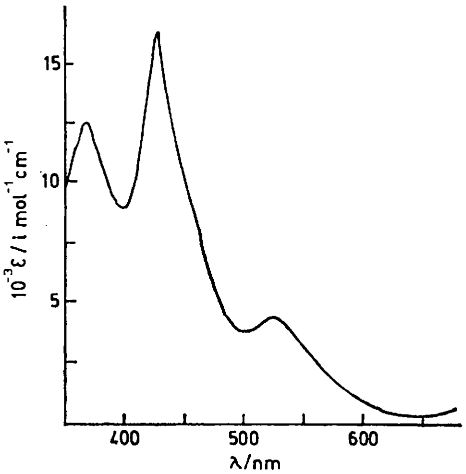

FIGURE 2 Visible spectrum of [Co(meab)] in ethanol at 25 °C

Spectral Changes in Mixed Aqueous Solvents.—Transition-metal complexes have been previously employed in solvent-structure studies. For example, Gillard and Sutton[12] investigated the spectral properties of bis(*meso*-stilbenediamine)nickel(II) acetate in a range of binary aqueous solvents. The establishment of a relation between the spectra of such salts and solvent structure is complicated by possible variations in the degree of ion association with the counter ion and by the existence of different co-ordination numbers for the metal centre in different solvents.[12] The complex [Co(meab)] has large enough ε values in the visible

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[12] R. D. Gillard and H. M. Sutton, *J. Chem. Soc.* (*A*), 1970, 1309.

region to offset its low solubility, and offers the dual advantages of stereochemical integrity and formal neutrality. The spectrum of this complex is a function of the availability of the solvent components at the probe.

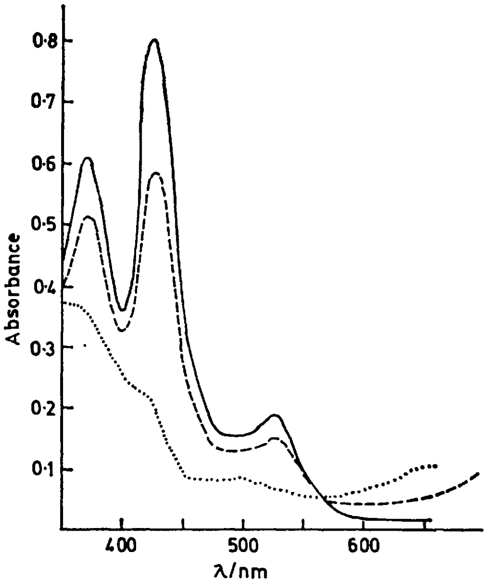

FIGURE 3 Spectra of [Co(meab)] (4.32×10^{-5}M) in aqueous solutions at different mol fractions of acetone and 25 °C, x = 0.259 (· · · ·), 0.423 (— — —), and 1 (——)

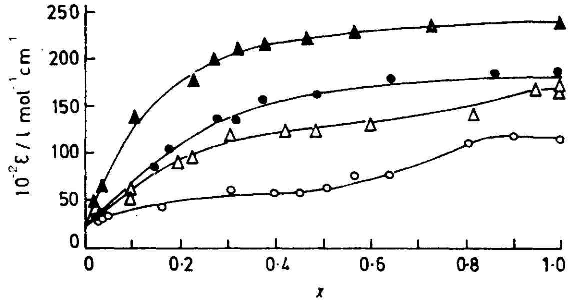

FIGURE 4 Variations in ε of [Co(meab)] as a function of mol fraction (x) of alcohol in binary mixed solvents at 25 °C and wavelengths: (○), water–methanol (421); (△), water–n-propanol (426); (●), water–ethanol (425); and (▲), water–t-butyl alcohol (428 nm)

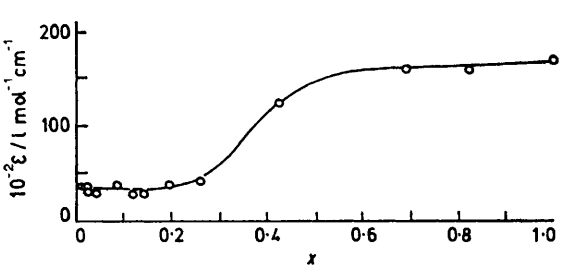

FIGURE 5 Values of ε at 428 nm for [Co(meab)] at different mol fractions (x) of acetone in aqueous acetone solvents at 25 °C

The spectral results for [Co(meab)] are illustrated in Figures 3—6. The spectra in Figure 3 were measured in aqueous mixtures containing different mol fractions (x) of acetone. The absorption maxima at x between 0.423 and 1 all appeared at the same wavelength and an isosbestic point was evident at 565 nm. These features persisted in other aqueous mixtures. Increasing x for alcohol caused ε to increase for all the aqueous alcohol solvents investigated, the effect being most marked for t-butyl alcohol (Figure 4); * however, ε for [Co(meab)] in aqueous acetone and pyridine at $x \leqslant 0.2$ (Figure 5) and $\leqslant 0.1$ (Figure 6) was very similar to that in pure water. These last two observations indicate that acetone and pyridine are not available to solvate [Co(meab)] up to these x limits {despite the fact that [Co(meab)] is more soluble in these two solvents than it is in water}, presumably because the added solvent components are ' buried ' in the one or more structures which the probe cannot distinguish from water. The absence of such clearly defined regions of constant ε at low x for alcohols suggests that some alcohol molecules are ' free ' to solvate [Co(meab)] under these conditions. Regions of constant ε at intermediate x of methanol and pyridine indicate the maintenance of other probe-indistinguishable solvent structures, and this may also be the case for n-propanol. Methanol is evidently more easily fitted into the prevailing water structure than are the other alcohols. Finally, ε is independent of increasing $x \geqslant$ 0.9, 0.6, 0.93, 0.3, 0.6, and 0.8 for methanol, ethanol, n-propanol, t-butyl alcohol, acetone, and pyridine, respectively, corresponding to the situation where water is effectively ' hidden ' in the prevailing co-solvent structures.

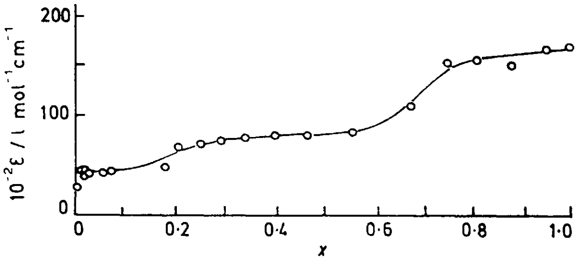

FIGURE 6 Values of ε at 434 nm for [Co(meab)] at different mol fractions (x) of pyridine in aqueous pyridine solvents at 25 °C

Measurements of thermodynamic, kinetic, electrical, and mechanical properties of water and mixed aqueous solvents have resulted in the postulation of several physical models for these systems.[1,2,13,14] Although the establishment of regions of apparently characteristic solvent structure depends to some extent on the characterization approach employed, there seems to be broad agreement that distinct solvent structural types exist at low and high mol fractions of alcohols in water.[2,13,14] Our results indicate that monohydric alcohols, except perhaps methanol, are free to solvate [Co(meab)] at

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* The same features due to solvent structural variations were observed at other wavelengths, although the magnitudes of the changes in ε were smaller and subject to greater experimental uncertainty.

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[14] E. S. Amis and J. F. Hinton, ' Solvent Effects on Chemical Phenomena,' Academic Press, New York, 1973.

$x < 0.1$. Wells[15] concluded that solvent structural changes in aqueous acetone take place at $x \sim 0.1$ and $x \sim 0.4$; the viscosity[16] of aqueous acetone is maximal at $x = 0.1$—0.15 and is almost constant at $x \geqslant 0.6$, the point at which the dielectric constant[17] becomes essentially invariant. Although we should not expect exact correspondence between the regions of apparent characteristic structure indicated by different measurements (see above), our spectrophotometric results support the conclusions of Wells to a reasonable degree and to that degree confirm the probe concept for [Co(meab)] (Figure 5). The intriguing results for aqueous pyridine (Figure 6) are difficult to interpret in the absence of extensive literature data, although a water–pyridine (2 : 1) clathrate has been detected[18] and hydrogen bonds between water molecules are apparently broken on addition of pyridine.[19] The [Co(meab)] complex experiences a characteristic structure encompassing pyridine–water mol ratios of *ca.* 0.5 to 2 : 1 with the exclusion of pyridine from this structure at $x \sim 0.8$.

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[5/131 *Received, 21st January,* 1975]

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