

## Studies of Chelation. Part 9.† Cobalt Complexes of 1-[(Substituted phenyl)azo]-2-naphthol and 1-[(Substituted phenylimino)methyl]-2-naphthol Ligands. Tautomerism and Reactivity

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Spectroscopic characterisation ( $^1\text{H}$  and  $^{13}\text{C}$  n.m.r., i.r., Raman, and u.v.-visible) of various 1-[(substituted phenyl)azo]-2-naphthols, R-Haz (R = 4'-Me, 4'-OMe, 4'-Cl, H, 2'-OMe, 2'-Me, 2'-Cl, and 2'-Br), and 1-[(substituted phenylimino)methyl]-2-naphthols, R-Hsb (R = 4'-OMe, 4'-Me, 4'-Cl, H, 4'-Br, 4'-CF<sub>3</sub>, 4'-CN, 4'-NO<sub>2</sub>, 2'-OMe, 2'-Me, 2'-CHMe<sub>2</sub>, 2'-Cl, 2'-CN, and 2'-NO<sub>2</sub>), in the solid state and in solution in both polar and non-polar solvents has shown that the hydrogen-bonded keto-tautomer is dominant in polar solvents. Reaction of cobalt(II) salts with R-Haz and with R-Hsb in ethanol produces [CoL<sub>2</sub>], *cis*-[Co(HL)<sub>2</sub>X<sub>2</sub>], and *fac*-[CoL<sub>3</sub>] (L = R-az or R-sb). The tautomeric form of the ligand in these complexes is established by vibrational spectroscopy and shown to be predominantly keto (hydrazone, ketoenamine) in [Co(R-az)<sub>2</sub>], in [Co(R-Haz)<sub>2</sub>X<sub>2</sub>], and [Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] (X = Cl or Br) but predominantly enolimine in [Co(R-sb)<sub>2</sub>]. The interconversion of [CoL<sub>2</sub>] and [Co(HL)<sub>2</sub>X<sub>2</sub>] is established generally: the intermediate, five-co-ordinate [Co(R-Hsb)(R-sb)X] is identified in certain cases (R = 4-OMe, 4-Me, or H). In the chelation process, proton loss follows ring closure and is succeeded by tautomerisation where this occurs. The facility with which the chelating ligand deviates from coplanarity of the benzene and naphthalene rings is a critical feature of the chelation process. The formation of [Co(R-az)<sub>3</sub>] from [Co(R-az)<sub>2</sub>] and from [Co(R-Haz)<sub>2</sub>X<sub>2</sub>] in the presence of air occurs easily and is acid catalysed. [Co(R-sb)<sub>3</sub>] is formed only under vigorously oxidising conditions. The isoelectronic ligands R-Haz and R-Hsb should not be regarded as identical in their reactivity towards cobalt(II).

ISOMERISM in the technically important 2:1 chromium(III) and cobalt(III) complexes [M(ABC)<sub>2</sub>] (M = Co or Cr) of tridentate 2,2'-dihydroxydiaryloazo-ligands, ABC, can arise in three distinct ways. The first, which is simply geometric, gives rise to 11 isomeric forms of which two have the ligand in the *mer* configuration and nine have the ligand co-ordinated facially.<sup>1</sup> The second arises from fluctuating co-ordination between the two nitrogen atoms of the azo-group and the metal ion.<sup>2</sup> The third is produced from the two non-planar configurations of the ligand in its hydrazone form, when the co-ordinated nitrogen is formally *sp*<sup>3</sup> hybridised.<sup>3</sup> Spectroscopic studies have shown that the different isomeric forms interconvert rapidly at ambient temperature in solution by intramolecular processes;<sup>1</sup> that is to say, without redistribution in the case of the unsymmetrical compound [M(ABC)(A'B'C')].

Substantial significance has been attached to comparisons between isoelectronic azomethine and azo-compounds, and the complexes which they form with a particular transition metal.<sup>4</sup>

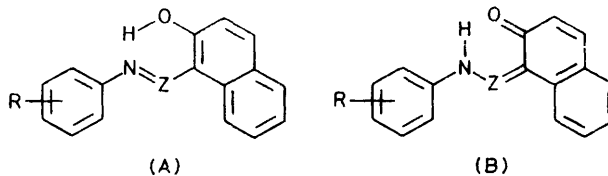
To examine this isomerism more closely because of its potential technological importance we have studied a group of 1-[(2'- or 4'-substituted phenyl)azo]-2-naphthols [(1), R-Haz], and the isoelectronic Schiff bases 1-[(2'- or 4'-substituted phenylimino)methyl]-2-naphthols [(2), R-Hsb], and the complexes which they form with cobalt(II) salts. The action of acid and of base on these complexes has been observed. We have chosen to work with bidentate ligands and to study the cobalt(II) complexes which they form in order to simplify the system as far as possible.

We shall show that there are significant differences between the complexes formed by the two types of

ligands and that a critical feature of the chelate ring closure process, which precedes proton loss, is the ease with which the ligand suffers distortion as a result of rotation.

### RESULTS AND DISCUSSION

1. *Ligand Tautomerism.*—Various analytical techniques have been used to determine the effect of solvent and of substituents on the azo-hydrazone equilibrium in 1-[(substituted phenyl)azo]-2-naphthols<sup>5</sup> [(1), Z = N]. Rather less attention has been given to the isoelectronic enolimine-ketoenamine [(2), Z = CH] tautomerism.



(1) Z = N azo (R-Haz) hydrazone  
(2) Z = CH enolimine (R-Hsb) ketoenamine

We have made a detailed comparison of the spectra of analogous compounds of both series in solution and in the solid state, with the following results.

(a) *Azomethine compounds.* The most significant  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. parameters for a selection of the 1-[(substituted phenylimino)methyl]-2-naphthols (2) and 1-[(substituted phenyl)azo]-2-naphthols (1) are given in Table 1, together with other data for comparison.

In the 2'-substituted azomethines, the methine proton resonance appears as a doublet; the splitting of this doublet increases with the electron-releasing character of the substituent. Most striking is the shift (*ca.* 6 p.p.m.) of both C(2) and C(12) in [(2), R = 2'-OMe],

† Part 8, J. A. Connor and G. A. Hudson, *J. Organomet. Chem.*, 1980, **185**, 385.

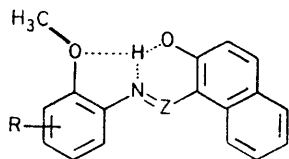
TABLE 1

Selected  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. chemical shifts  $\delta$  (p.p.m.) for 1,2-disubstituted naphthalenes in  $\text{CDCl}_3$  solution (ca.  $0.25 \text{ mol dm}^{-3}$ )

|                            |                      | C(1)   | C(2)   | C(11)H | C(11)H                  | C(12)  | Ref. |
|----------------------------|----------------------|--------|--------|--------|-------------------------|--------|------|
| 1,2-Naphthoquinone         |                      | 179.8  | 180.9  |        |                         |        | a    |
| 2-Naphthol                 |                      | 109.61 | 153.35 |        |                         |        | b    |
| 2-Hydroxy-1-naphthaldehyde |                      | 111.06 | 164.57 | 192.87 | 10.56                   |        | c    |
| 1-Chloro-2-naphthol        |                      | 113.37 | 149.40 |        |                         |        | d    |
| R-Haz                      | R                    |        |        |        |                         |        |      |
|                            | 4'-OMe               | 121.68 | 161.19 |        |                         | 141.94 | c    |
|                            | 4'-Me                | 121.60 | 167.70 |        |                         | 143.85 | c    |
|                            | 2'-OMe               | 116.36 | 176.85 |        |                         | 149.99 | c    |
|                            | 2'-Me                | 124.89 | 172.10 |        |                         | 143.15 | c    |
| R-Hsb                      | R                    |        |        |        |                         |        |      |
|                            | 4'-OMe               | 109.09 | 168.88 | 154.06 | 9.25                    | 139.06 | c    |
|                            | 4'-Me                | 108.72 | 170.63 | 153.65 | 9.18                    | 142.46 | c    |
|                            | 4'-Cl                | 109.30 | 168.21 | 156.31 | 9.20                    | 145.32 | c    |
|                            | 4'-NO <sub>2</sub>   | 109.49 | 169.01 | 157.35 | 9.36                    | 152.25 | c    |
|                            | 2'-OMe               | 108.57 | 177.26 | 149.69 | 9.10 (8.0) <sup>e</sup> | 151.21 | c    |
|                            | 2'-Me                | 108.80 | 171.29 | 153.50 | 9.26 (4.7)              | 143.48 | c    |
|                            | 2'-CHMe <sub>2</sub> | 109.16 | 169.16 | 155.63 | 9.22 (4.0)              | 143.77 | c    |
|                            | 2'-Cl                | 109.30 | 168.82 | 155.68 | 9.28 (3.0)              | 143.37 | c    |
|                            | 2'-NO <sub>2</sub>   | 109.97 | 168.87 | 157.02 | 9.34 (2.7)              | 142.02 | c    |

<sup>a</sup> I. A. McDonald, T. J. Simpson, and A. F. Sierakowski, *Aust. J. Chem.*, 1977, **30**, 1727. <sup>b</sup> L. Ernst, *Chem. Ber.*, 1975, **108**, 2030. <sup>c</sup> This work. <sup>d</sup> N. K. Wilson and R. D. Zehr, *J. Org. Chem.*, 1978, **43**, 1768. <sup>e</sup>  $^1\text{J}(\text{CH})/\text{Hz}$  in parentheses.

when compared with other 1-[(2'-substituted phenylimino)methyl]-2-naphthols. When other electron-donating 2'-substituents [(2), R = 2'-Me or 2'-CHMe<sub>2</sub>] are considered, it would appear that the shift to lower field of both these carbon atoms C(2) and C(12) in [(1) and (2), R = 2'-OMe] is the result of the bifurcated hydrogen-bond structure shown below in which annelation of a



five- and a six-membered ring occurs. There is no evidence for stabilisation of the hydrogen bond by the formation of two six-membered rings which might have occurred in [(2), R = 2'-NO<sub>2</sub>].

In the 4'-substituted series, the methine proton resonance is a single, broad signal. Spectroscopic data suggest that these compounds exist mainly in the enolimine (2A) form in a weakly polar solvent ( $\text{CDCl}_3$ ) and in the solid state, but the equilibrium shifts in

TABLE 2

Effect of solvent polarity on  $^1\text{H}$  n.m.r. chemical shifts  $\delta$  (p.p.m.) of 1-[(substituted phenylimino)methyl]-2-naphthols, R-Hsb

| R                  | $\delta$ (OH/NH) | $\delta$ [C(11)H] | $\delta$ (H <sup>8</sup> ) | Solvent |
|--------------------|------------------|-------------------|----------------------------|---------|
| 2'-NO <sub>2</sub> | 14.54            | 9.34              | 8.10                       | a       |
|                    | 14.58            | 9.54              | 8.43                       | b       |
| 2'-Cl              | 15.30            | 9.40              | 8.19                       | a       |
|                    | 15.54            | 9.58              | 8.41                       | b       |
| 2'-OMe             | 15.60            | 9.10              | 7.93                       | a       |
|                    | 15.75            | 9.45              | 8.37                       | b       |
| 4'-NO <sub>2</sub> | 14.78            | 9.36              | 8.09                       | a       |
|                    | <sup>c</sup>     | 9.62              | 8.48                       | b       |
| 4'-Cl              | 15.05            | 9.28              | 8.08                       | a       |
|                    | 15.48            | 9.58              | 8.43                       | b       |
| 4'-OMe             | 15.56            | 9.25              | 8.05                       | a       |
|                    | 15.87            | 9.43              | 8.33                       | b       |

<sup>a</sup>  $\text{CDCl}_3$ . <sup>b</sup>  $(\text{CD}_3)_2\text{SO}$ . <sup>c</sup> Not observed.

favour of the ketoenamine form (2B) in a polar protic solvent (ethanol). The 2'-substituted azomethine derivatives exist mainly in the ketoenamine (2B) form in both weakly polar and polar protic solvents, and also in the solid state. The influence of solvent polarity is also manifest (Table 2) in the  $^1\text{H}$  n.m.r. spectra of the azomethine ligands recorded in both  $\text{CDCl}_3$  and  $[\text{D}_6\text{H}_6]\text{dmsO}$  (dmsO = dimethyl sulphoxide). The shift to lower field in the more polar solvent is greater for the 4'-substituted ligands than for the 2'-substituted series.

(b) *Azo-compounds*. The compounds of the 2'-substituted series (1) can be distinguished from those of the 4'-substituted series by the observation of a doublet ( $^3J$  8 Hz) centred at  $\delta$  8.1 p.p.m. in the  $^1\text{H}$  n.m.r. spectra of the former; this signal is due to H<sup>5</sup> on the naphthalene ring. The observation of this signal is consistent with the dominance of the azo-tautomer (1A) in solutions of the 2'-substituted phenyl series in weakly polar solvents. This is confirmed by a decrease in the separation between the doublet due to H<sup>8</sup> ( $^3J$  8 Hz) centred at  $\delta$  8.5 p.p.m. and the aromatic proton multiplet from 60–66 Hz in the 4'-substituted series to 50–56 Hz in the 2'-substituted series.

All the 1-[(substituted phenyl)azo]-2-naphthol derivatives show a broad signal at  $\delta$  ca. 16 p.p.m., which is due to the exchangeable hydrogen-bonded hydroxyl/aminyl proton. From the position of the signal, hydrogen bonding would appear to be strongest in [(1), R = 2'-OMe] ( $\delta$  16.53 p.p.m.) and weakest in [(1), R = 4'-OMe] ( $\delta$  15.60 p.p.m.); we have observed <sup>6</sup> exactly similar substituent effects in the position of the OH/NH resonance of 2-[(2'- and 4'-substituted phenyl)azo]-4-methylphenol compounds which are assumed <sup>7</sup> to exist entirely in the azo-form, although exchange <sup>8</sup> between the azo and hydrazone tautomers is fast ( $\tau > 10^4 \text{ s}^{-1}$ ) at 150 K.

The i.r. (solid mulls) and electronic spectra (ethanol) confirm the view that the 1-[(4'-substituted phenyl)azo]-2-naphthol compounds exist principally in the

hydrazone form in these media.<sup>9</sup> The 2'-substituted analogues exist in the azo-form (1A) in a weakly polar solvent (chloroform) and as equilibrium mixtures with a slight preference for the hydrazone form in ethanol solution and in the solid state. Crystallographic studies of various 1-[(2'- and 4'-substituted phenyl)azo]-2-naphthols have confirmed the *o*-quinonoid, hydrazone structure in the solid state; however, the location of the hydroxyl/aminyl proton has not been established.<sup>10</sup>

The strength of the hydrogen bonding in the azomethine (2) series is less than in the corresponding azo-compounds (1), and is dependent upon both the position (2' > 4') and the nature (OMe > NO<sub>2</sub>) of the substituent on the phenyl ring. In strictly comparable cases, there is evidence<sup>11</sup> to suggest that the azomethine ligand [*e.g.* (2), R = 4'-OMe; p*K*<sub>a</sub>(OH) 10.96] is a stronger acid than the corresponding azo-ligand [*e.g.* (1), R = 4'-OMe; p*K*<sub>a</sub>(OH) 12.64].

Almost all of the complexes of cobalt with the ligands R-Haz (1) and R-Hsb (2) which are described in the next section are prepared in ethanol solution, in which the ketonic tautomer (1B, 2B) is present in higher concentration than the enol tautomer (1A, 2A).

2. *Complexes of Azo-ligands, R-Haz.*—Previous work has shown<sup>12</sup> that R-Haz (R = 4'-OMe, 4'-Me, or H) react with cobalt(II) acetate to form neutral, dark green, high-spin ( $\mu_{\text{eff}}$  4.3–4.5 B.M.\* at 295 K), tetrahedral complexes, [Co(R-az)<sub>2</sub>]. No complex is formed when R is an electron-attracting substituent. The same ligands, R-Haz (R = 4'-OMe, 4'-Me, or H), react with cobalt(II) halides CoX<sub>2</sub> (X = Cl or Br) in ethanol to form neutral, reddish brown, high-spin ( $\mu_{\text{eff}}$  5.0–5.2 B.M. at 295 K) octahedral complexes [Co(R-Haz)<sub>2</sub>X<sub>2</sub>]. The azo-ligands, R-Haz (R = 4'-OMe, 4'-Me, or H), react with Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] in ethanol to form dark blue octahedral *fac*-[Co(R-az)<sub>3</sub>].

Addition of hydrochloric acid (2 mol) to [Co(R-az)<sub>2</sub>] (R = H) in dry deoxygenated ethanol gives [Co(R-Haz)<sub>2</sub>Cl<sub>2</sub>] (R = H) if the acid is added slowly; too rapid addition causes disintegration of the complex and liberation of H-Haz. Addition of potassium acetate (2 mol) to [Co(R-Haz)<sub>2</sub>Cl<sub>2</sub>] (R = H) in dry ethanol at reflux produced [Co(R-az)<sub>2</sub>] (R = H) after 0.5 h, but if the period of reflux is extended (24 h) the product is *fac*-[Co(R-az)<sub>3</sub>] (R = H). When the same reaction with potassium acetate is carried out under strict anaerobic conditions no cobalt(III) complex is formed even after 36 h at reflux. Addition of potassium acetate (1 mol) to an ethanol solution of [Co(R-Haz)<sub>2</sub>Cl<sub>2</sub>] (R = H, 1 mol) and refluxing for 2 h produced [Co(R-az)<sub>2</sub>] (R = H), and on leaving the filtrate obtained from the reaction to stand in air overnight *fac*-[Co(R-az)<sub>3</sub>] (R = H) was formed. Finally, [Co(R-az)<sub>2</sub>] (R = H, 1 mol) is oxidised to *fac*-[Co(R-az)<sub>3</sub>] (R = H) by the reaction of hydrochloric acid (0.1 mol) in aerated ethanol at reflux (1 h). Further clarification of the acid-catalysed oxidation of [Co(R-az)<sub>2</sub>] (R = H) is provided by the observation that [Co(R-az)<sub>2</sub>] (R = H) does not react with R-Haz (R = H) (1 : 1) in

\* Throughout this paper: 1 B.M.  $\approx 9.27 \times 10^{-24}$  A m<sup>2</sup>.

refluxing aerated ethanol, nor on refluxing alone in aerated ethanol to form *fac*-[Co(R-az)<sub>3</sub>] (R = H), but the cobalt(III) complex is formed rapidly when an aerated ethanolic solution containing equimolar amounts of both [Co(R-az)<sub>2</sub>] (R = H) and [Co(R-Haz)<sub>2</sub>Cl<sub>2</sub>] (R = H) is heated at reflux.

It seems that the loss of HX resulting from the addition of K[O<sub>2</sub>CCH<sub>3</sub>] to a solution of [Co(R-Haz)<sub>2</sub>X<sub>2</sub>] causes an increase in the acidity of the mixture which is sufficient to change the redox potential,  $E^{\circ}\{[\text{Co}(\text{R-az})_3]/[\text{Co}(\text{R-az})_2], \text{R-Haz}\}$  in favour of the cobalt(III) complex. Normally, an increase in the acidity of a system involving proton loss could be expected to favour the lower oxidation state. In this case it would seem that both oxygen and H<sup>+</sup> are involved as oxidation only takes place if both are present.

With the exception of (R-Haz, R = 2'-OMe), no cobalt complex can be isolated when 1-[(2'-substituted phenyl)azo]-2-naphthols are used as ligands. It seems likely that this complex [Co(R-az)<sub>2</sub>] (R = 2'-OMe) ( $\mu_{\text{eff}}$  4.30 B.M.) is stabilised by a weak interaction between the methoxy-group and the cobalt atom. An interaction of this kind is known<sup>13</sup> in the complex [Cu(R-az)Cl] (R = 2'-OMe).

The i.r. and Raman spectra<sup>6</sup> of the complexes generally show a marked sharpening of the absorptions compared with those of the free ligand. The broad absorption at *ca.* 1550 cm<sup>-1</sup> in the free ligand R-Haz which is assigned to a combination of vibrations involving NH bending and -N=C stretching of the (NH-N=C) group associated with the hydrazone tautomer (1B) appears as a sharp, strong absorption at *ca.* 1545 cm<sup>-1</sup> in the spectra of the complexes. This would seem to indicate that the ligands co-ordinated to the cobalt atom maintain the hydrazone structure. The vibration  $\nu(\text{N}=\text{N})$ , identified as contributing to the strong absorption at 1380 cm<sup>-1</sup> in the Raman spectrum of R-Haz (R = 4'-Me), is not observed in the Raman spectrum of [Co(R-az)<sub>2</sub>], which is consistent with a shift of the tautomeric equilibrium in favour of the hydrazone form on co-ordination. We were most surprised not to observe any strong absorption below 400 cm<sup>-1</sup> in the i.r. and Raman spectra of the octahedral [Co(R-Haz)<sub>2</sub>X<sub>2</sub>] complexes, despite a number of attempts to do so with a variety of different samples of analytically pure material. The lack of any observation of  $\nu(\text{Co-X})$  precludes the identification of the geometry of the [Co(R-Haz)<sub>2</sub>X<sub>2</sub>] complexes; however, the fact that these complexes are readily converted to *fac*-[Co(R-az)<sub>3</sub>] suggests that they may have the *cis* configuration, as have the [Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] complexes which will be described below.

3. *Complexes of Azomethine Ligands, R-Hsb.*—It was generally found advantageous to work in an inert (deoxygenated nitrogen gas) atmosphere and to use deoxygenated solvents in the preparation of these complexes. Previous work has described<sup>14</sup> the complexes of cobalt formed by 2-[(substituted phenylimino)methyl]-phenols. In order to maintain the closest possible comparability with the azo-ligand systems already

described, we have used a series of 1-[(substituted phenylimino)methyl]-2-naphthols, R-Hsb.

Cobalt(II) acetate reacts with R-Hsb (R = H, 4'-OMe, 4'-Me, 4'-Cl, 4'-Br, 4'-CF<sub>3</sub>, 4'-CN, 4'-NO<sub>2</sub>, 2'-OMe, 2'-CHMe<sub>2</sub>, and 2'-Cl) in methanol to form paramagnetic ( $\mu_{\text{eff}} = 4.0\text{--}4.2$  B.M. at 295 K), neutral red tetrahedral complexes, [Co(R-sb)<sub>2</sub>] (see Table 3). We have been unable to prepare a complex from R-Hsb (R = 2'-CN, 2'-NO<sub>2</sub>) despite various attempts to do so: the reason for this is not apparent. Previously, complexes of ligands bearing a substituent in the 2'-position on the phenyl ring have been reported<sup>15</sup> to be exceedingly difficult or impossible to prepare and unfavourable steric effects were blamed. Our experience would indicate that the solubility of the components in the reaction medium and the need for anaerobic conditions are the dominant influences. The ligand in these [Co(R-sb)<sub>2</sub>] complexes is present in the enolimine tautomeric form. The evidence for this is provided by a shift (10—20 cm<sup>-1</sup>) of the absorption assigned to  $\nu(\text{Ph} + \text{C}=\text{N})$  and  $\nu(\text{C} \rightleftharpoons \text{C})$  to lower wavenumbers, and a shift (30 cm<sup>-1</sup>) of the absorption assigned to the naphtholic C—O stretching vibration to higher wavenumbers.

Addition of a solution of any anhydrous cobalt(II) halide, CoX<sub>2</sub> (X = Cl or Br), in dry ethanol to a refluxing solution of R-Hsb (R = H, 4'-OMe, 4'-Me, 4'-Cl, 4'-Br, 4'-CF<sub>3</sub>, 3'-Me, 2'-Me, and 2'-CHMe<sub>2</sub>) results in the formation of neutral, green, high-spin ( $\mu_{\text{eff}}$ , 4.9—5.2 B.M. at 295 K) octahedral complexes [Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] in which

TABLE 3  
[Co(R-sb)<sub>2</sub>] complexes

| (a) Analyses                    |                                                                                 | Analysis (%) <sup>a</sup> |              |                |              |
|---------------------------------|---------------------------------------------------------------------------------|---------------------------|--------------|----------------|--------------|
| R                               | Empirical formula                                                               | C                         | H            | Co             | N            |
| 4'-OMe                          | C <sub>36</sub> H <sub>28</sub> CoN <sub>2</sub> O <sub>4</sub>                 | 71.5<br>(70.7)            | 4.7<br>(4.6) | 10.5<br>(9.6)  | 4.3<br>(4.6) |
| 4'-Me                           | C <sub>36</sub> H <sub>28</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 74.7<br>(74.6)            | 4.9<br>(4.8) | 9.9<br>(10.2)  | 5.0<br>(4.8) |
| H                               | C <sub>34</sub> H <sub>24</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 73.8<br>(74.1)            | 4.5<br>(4.4) | 10.2<br>(10.7) | 5.4<br>(5.1) |
| 4'-Cl <sup>b</sup>              | C <sub>34</sub> H <sub>22</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub> | 66.6<br>(65.8)            | 3.6<br>(3.6) | 9.0<br>(9.5)   | 4.4<br>(4.5) |
| 4'-Br <sup>c</sup>              | C <sub>34</sub> H <sub>22</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub> | 57.5<br>(57.6)            | 3.3<br>(3.1) | 8.2<br>(8.3)   | 3.8<br>(4.0) |
| 4'-CF <sub>3</sub> <sup>d</sup> | C <sub>36</sub> H <sub>22</sub> CoF <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 63.0<br>(62.9)            | 3.2<br>(3.2) | 8.4<br>(8.6)   | 4.1<br>(4.1) |
| 4'-CN                           | C <sub>36</sub> H <sub>22</sub> CoN <sub>4</sub> O <sub>2</sub>                 | 72.4<br>(71.9)            | 4.0<br>(3.7) | 9.7<br>(9.8)   | 9.6<br>(9.3) |
| 4'-NO <sub>2</sub>              | C <sub>34</sub> H <sub>22</sub> CoN <sub>4</sub> O <sub>6</sub>                 | 65.0<br>(63.7)            | 3.5<br>(3.4) | 8.9<br>(9.2)   | 8.9<br>(8.7) |
| 2'-OMe                          | C <sub>36</sub> H <sub>28</sub> CoN <sub>2</sub> O <sub>4</sub>                 | 69.8<br>(70.7)            | 4.6<br>(4.6) | 10.0<br>(9.6)  | 4.5<br>(4.6) |
| 2'-CHMe <sub>2</sub>            | C <sub>40</sub> H <sub>36</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 75.5<br>(75.6)            | 5.8<br>(5.7) | 9.2<br>(9.3)   | 4.2<br>(4.4) |
| 2'-Cl <sup>e</sup>              | C <sub>34</sub> H <sub>22</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub> | 65.4<br>(65.8)            | 3.6<br>(3.5) | 8.9<br>(9.5)   | 4.1<br>(4.5) |

(b) Magnetic moment (295 K) and conductivity in nitroethane solution

| R                    | $\mu_{\text{eff.}}$ /B.M. | $\Lambda$ /S cm <sup>2</sup> mol <sup>-1</sup> |
|----------------------|---------------------------|------------------------------------------------|
| 4'-OMe               | 4.21                      | < 1                                            |
| H                    | 4.03                      | < 1                                            |
| 4'-Cl                | 4.22                      | < 1                                            |
| 2'-CHMe <sub>2</sub> | 4.03                      | < 1                                            |

<sup>a</sup> Found (calc.). <sup>b</sup> Cl: Found 11.1, calc. 11.5%. <sup>c</sup> Br: Found 22.8, calc. 22.5%. <sup>d</sup> F: Found 16.9, calc. 16.6%. <sup>e</sup> Cl: Found 11.6, calc. 11.5%.

TABLE 4  
Characterization of *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] complexes  
(a) Analytical data<sup>a</sup> for X = Cl

| R                               | Empirical formula                                                                               | Analysis (%)   |              |                |              |              |
|---------------------------------|-------------------------------------------------------------------------------------------------|----------------|--------------|----------------|--------------|--------------|
|                                 |                                                                                                 | C              | H            | Cl             | Co           | N            |
| 4'-OMe                          | C <sub>36</sub> H <sub>30</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>4</sub>                 | 63.8<br>(63.2) | 4.5<br>(4.4) | 10.3<br>(10.4) | 8.3<br>(8.6) | 3.9<br>(4.1) |
| 4'-Me                           | C <sub>36</sub> H <sub>30</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 66.0<br>(66.3) | 4.5<br>(4.6) | 10.9<br>(10.9) | 9.1<br>(9.0) | 3.9<br>(4.3) |
| H                               | C <sub>34</sub> H <sub>26</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 65.4<br>(65.4) | 4.1<br>(4.2) | 11.3<br>(11.4) | 9.2<br>(9.4) | 4.2<br>(4.5) |
| 4'-Cl                           | C <sub>34</sub> H <sub>24</sub> Cl <sub>4</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 58.2<br>(58.9) | 3.8<br>(3.5) | 19.2<br>(20.5) | 8.3<br>(8.5) | 3.8<br>(4.0) |
| 4'-Br <sup>b</sup>              | C <sub>34</sub> H <sub>24</sub> Br <sub>2</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub> | 52.0<br>(52.5) | 3.0<br>(3.1) | 9.3<br>(9.1)   | 7.5<br>(7.5) | 3.5<br>(3.6) |
| 4'-CF <sub>3</sub> <sup>c</sup> | C <sub>36</sub> H <sub>24</sub> Cl <sub>2</sub> CoF <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 57.0<br>(56.8) | 3.5<br>(3.2) | 9.0<br>(9.3)   | 7.4<br>(7.8) | 3.6<br>(3.7) |
| 2'-Me                           | C <sub>36</sub> H <sub>30</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 66.7<br>(66.3) | 4.5<br>(4.6) | 10.3<br>(10.9) | 8.9<br>(9.0) | 4.0<br>(4.3) |
| 2'-CHMe <sub>2</sub>            | C <sub>40</sub> H <sub>38</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 66.6<br>(67.8) | 5.5<br>(5.4) | 10.0<br>(10.0) | 8.0<br>(8.3) | 3.8<br>(4.0) |

(b) Analytical data<sup>a</sup> for X = Br

| R                    | Empirical formula                                                                               | Analysis (%)   |              |                |              |              |
|----------------------|-------------------------------------------------------------------------------------------------|----------------|--------------|----------------|--------------|--------------|
|                      |                                                                                                 | C              | H            | Br             | Co           | N            |
| 4'-OMe               | C <sub>36</sub> H <sub>30</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>4</sub>                 | 56.1<br>(55.9) | 4.0<br>(3.9) | 20.5<br>(20.7) | 7.9<br>(7.6) | 3.4<br>(3.6) |
| 4'-Me                | C <sub>36</sub> H <sub>30</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 56.7<br>(58.3) | 4.0<br>(4.1) | 21.3<br>(21.6) | 8.0<br>(8.0) | 3.6<br>(3.8) |
| H                    | C <sub>34</sub> H <sub>26</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 57.0<br>(57.2) | 3.5<br>(3.6) | 22.4<br>(22.4) | 8.0<br>(8.3) | 3.8<br>(3.9) |
| 4'-Cl <sup>d</sup>   | C <sub>34</sub> H <sub>24</sub> Br <sub>2</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub> | 51.9<br>(52.2) | 3.1<br>(3.1) | 20.3<br>(20.4) | 7.5<br>(7.5) | 3.5<br>(3.6) |
| 4'-Br                | C <sub>34</sub> H <sub>24</sub> Br <sub>4</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 46.6<br>(46.8) | 2.8<br>(2.8) | 35.3<br>(36.7) | 6.5<br>(6.8) | 3.1<br>(3.2) |
| 2'-Me                | C <sub>36</sub> H <sub>30</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 58.4<br>(58.3) | 4.2<br>(4.1) | 21.8<br>(21.6) | 7.7<br>(7.9) | 3.7<br>(3.8) |
| 2'-CHMe <sub>2</sub> | C <sub>40</sub> H <sub>38</sub> Br <sub>2</sub> CoN <sub>2</sub> O <sub>2</sub>                 | 60.3<br>(60.2) | 4.8<br>(4.8) | 19.9<br>(20.1) | 7.4<br>(7.4) | 3.4<br>(3.5) |

(c) Magnetic moment (295 K) and solution conductivity

| R                    | X  | $\mu_{\text{eff.}}$ /B.M. | $\Lambda$ (dmf)/S cm <sup>2</sup> mol <sup>-1</sup> | $\Lambda$ (EtNO <sub>2</sub> )/S cm <sup>2</sup> mol <sup>-1</sup> |
|----------------------|----|---------------------------|-----------------------------------------------------|--------------------------------------------------------------------|
| 4'-OMe               | Cl | 4.90                      | 27.3                                                | 9.1                                                                |
| 4'-OMe               | Br | 5.24                      | 46.1                                                | 12.0                                                               |
| 4'-Me                | Cl | 5.24                      | 10.4                                                | 2.0                                                                |
| H                    | Cl | 5.10                      | 6.2                                                 | 2.4                                                                |
| 4'-CF <sub>3</sub>   | Cl | 5.03                      | 43.7                                                | 10.0                                                               |
| 2'-CHMe <sub>2</sub> | Cl | 5.09                      | 8.0                                                 | 3.6                                                                |
| 2'-Me                | Cl | 5.01                      | 16.3                                                | 12.2                                                               |

<sup>a</sup> Found (calc.). <sup>b</sup> Br: Found 21.0; calc. 20.4%. <sup>c</sup> F: Found 14.9; calc. 15.0%. <sup>d</sup> Cl: Found 9.0; calc. 9.1%.

no proton loss from the ligand occurs (Table 4). Attempts to prepare complexes from the ligands R-Hsb (R = 2'-CN, 2'-NO<sub>2</sub>, 4'-CN, or 4'-NO<sub>2</sub>) were unsuccessful. The i.r. and Raman spectra<sup>6</sup> of these cobalt(II) complexes are consistent with an increase in the ketoenamine character in the co-ordinated azomethine ligand in the [Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] complexes compared to the tetrahedral [Co(R-sb)<sub>2</sub>] complexes. The vibrational spectra of [Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] also contain *two* strong absorptions at 330 and 290 cm<sup>-1</sup> (X = Cl) and 260 and 240 cm<sup>-1</sup> (X = Br), which are assigned to  $\nu(\text{Co-X})$  and indicate a *cis* stereochemistry for the halogen ligands.

The red tetrahedral [Co(R-sb)<sub>2</sub>] (R = 4'-OMe, 4'-Me, or 4'-Cl) complexes react with acid, HX (X = Cl, Br) (2 mol), in dry ethanol to give the green octahedral *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>]. The addition of base (potassium acetate, 2 mol) to *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] in ethanol and heating at reflux for 1 h produces [Co(R-sb)<sub>2</sub>] in high

yield. However, when only *one* mol of potassium acetate was added to a stirred, refluxing solution of *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] (R = 4'-OMe or 4'-Me; X = Cl or Br) in the minimum amount of dry ethanol required to effect solution, dark purple crystals were deposited from the reaction during 15 h. These crystals could be ground to a dark brown powder. Elemental analysis, the magnetic moment of the solid ( $\mu_{\text{eff}}$ , 3.47 B.M. at 295 K, R = 4'-Me, X = Br), and the very low molar conductivity in dmf (dimethylformamide) solution are consistent with a five-coordinate cobalt(II) species. The i.r. spectra of these purple species are very complex. Bands characteristic of both enolimine {as in [Co(R-sb)<sub>2</sub>]} and ketoenamine {as in *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>]} forms of the ligand are observed. In the low frequency region *only one* strong band is observed at 315 cm<sup>-1</sup> (X = Cl) or 240 cm<sup>-1</sup> (X = Br). This fact together with the observation that the pattern of relative intensities of i.r. absorptions in the region 625—1 700 cm<sup>-1</sup> is *not* well reproduced by a 1 : 1 mixture of [Co(R-sb)<sub>2</sub>] and *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>], establish that these purple complexes are discrete compounds having the constitution [Co(R-sb)(R-Hsb)X]. The diffuse reflectance spectra indicate (Table 5) that

TABLE 5

Diffuse reflectance spectra of [Co(R-sb)<sub>2</sub>], *cis*-[Co(R-Hsb)<sub>2</sub>Br<sub>2</sub>], and [Co(R-Hsb)(R-sb)Br] (R = 4'-OMe or 4'-Me) complexes

| Complex                                                    | $\bar{\nu}/\text{cm}^{-1}$                      |
|------------------------------------------------------------|-------------------------------------------------|
| [Co(4'-Me-sb) <sub>2</sub> ]                               | 7 300, 8 800, 11 000, 16 700,<br>20 600, 21 800 |
| [Co(4'-OMe-sb) <sub>2</sub> ]                              | 7 500, 9 100, 11 000, 16 700,<br>18 300, 21 200 |
| <i>cis</i> -[Co(4'-Me-Hsb) <sub>2</sub> Br <sub>2</sub> ]  | 5 100, 5 900, 7 300, 15 400,<br>21 600          |
| <i>cis</i> -[Co(4'-OMe-Hsb) <sub>2</sub> Br <sub>2</sub> ] | 5 200, 6 100, 7 500, 16 000,<br>21 400          |
| [Co(4'-Me-Hsb)(4'-Me-sb)Br]                                | 4 500, 6 800, 8 000, 10 100,<br>17 500, 21 900  |
| [Co(4'-OMe-Hsb)(4'-OMe-sb)Br]                              | 4 700, 7 000, 8 400, 10 700,<br>17 900, 22 500  |

the complexes [Co(R-sb)(R-Hsb)X] are distinguishable from [Co(R-sb)<sub>2</sub>] and *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>].

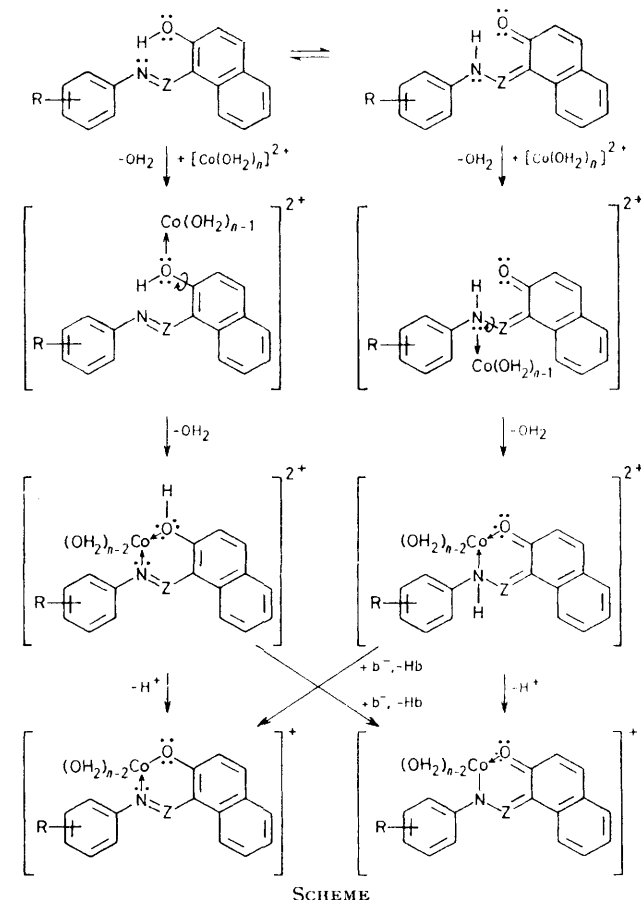
The cobalt(II) complexes *cis*-[Co(R-Hsb)<sub>2</sub>X<sub>2</sub>] are not oxidised to cobalt(III) complexes {e.g. [Co(R-sb)<sub>3</sub>]} by the action of potassium acetate or by the combined action of acid and air on [Co(R-sb)<sub>2</sub>]. The tris-(ligand) complexes can be prepared by the action of hydrogen peroxide (100 vol.%) on a mixture of R-Hsb and [Co(R-sb)<sub>2</sub>] in ethanol at reflux. The <sup>1</sup>H n.m.r. spectrum of [Co(R-sb)<sub>3</sub>] (R = 4'-Me) shows three methyl resonances ( $\delta$  1.70, 2.05, and 2.20), indicative of a *fac* configuration of the ligands.

#### 4. Comparison of Azo and Azomethine Complexes.—

In considering the complexes formed by the ligands R-Haz and R-Hsb with cobalt(II) the following points need to be borne in mind. In ethanol solution, the ligands 4'-R-Hsb, 4'-R-Haz, and 2'-R-Hsb all exist predominantly as the ketonic tautomer, but this tautomer is only slightly favoured in the case of 2'-R-Haz. All of these ligands exist as intramolecular hydrogen-bonded

structures in solution; the strength of this hydrogen bonding generally decreases in the order 2'-R-Haz > 4'-R-Haz > 2'-R-Hsb > 4'-R-Hsb. It is known that azobenzene is planar both in the gas phase and in the solid state.<sup>16</sup> [(Phenylimino)methyl]benzene is not planar, the torsion angle about the phenyl(C)-N bond is 35—55°, depending on the phase.<sup>17</sup> We suggest that twisting of the phenyl ring about the C-N bond will also occur in the 1-[(substituted phenylimino)methyl]-2-naphthols we have used. This deformation is expected to occur more easily in the ketoenamine tautomer. Simple models of [CoL<sub>2</sub>] and *cis*-[Co(HL)<sub>2</sub>X<sub>2</sub>] (L = 2'- or 4'-R-az and 2'- or 4'-R-sb) suggest that twisting of the phenyl ring relative to the naphthalene ring will favour co-ordination.

Although the synthesis of the cobalt(II) complexes of both R-Haz and R-Hsb is carried out in neutral ethanol solution, in which the keto-tautomer of the ligand is present in higher concentration than the enol tautomer, it is important to recognise that both tautomers are present and that co-ordination of the metal can originate from either tautomer of each ligand. This is indicated by the Scheme. The Scheme emphasises first, that rotation of the singly co-ordinated ligand about the C(2)-OH bond (enol) or the Z-NH bond (keto) must precede chelation; secondly, that proton loss follows chelation; and thirdly, that tautomerisation of the



chelated ligand may be assisted by proton loss in the presence of a base (*e.g.* acetate).

Protonation of the ligand which occurs when  $[\text{CoL}_2]$  ( $L = \text{R-az}$ ,  $\text{R-sb}$ ) is treated with acid to form  $\text{cis-}[\text{Co}(\text{HL})_2\text{X}_2]$  will most likely occur at nitrogen rather than oxygen. When cobalt(II) acetate reacts with HL, the product is  $[\text{CoL}_2]$ , but when cobalt(II) halides are used, the product is  $[\text{Co}(\text{HL})_2\text{X}_2]$ . This is consistent with the greater basicity of the acetate ion compared with halide ion, and indicates that the  $\text{p}K_a$  of the coordinated ligand, HL, in  $[\text{Co}(\text{HL})_2\text{X}_2]$  is less than that of acetic acid ( $\text{p}K_a$  4.75) and greater than that of the hydrohalogenic acid. In this context, we note that the acidity of 2-hydroxybenzoic (salicylic) acid [ $\text{p}K_a(\text{OH})$  13.2] is less than that of its complex  $[\text{Co}(\text{en})_2(\text{Hsal})]^{2+}$  [ $\text{p}K_a(\text{OH})$  1.80].<sup>18</sup>

It appears that failure to prepare complexes of 2'-R-Haz can be seen as the consequence of two unfavourable factors: the relatively high concentration of the hydroxyazo-tautomer (1A) and the strength of hydrogen bonding in a planar system.

The difference in the effect of substituents, which is apparent in the series of  $[\text{CoL}_2]$  ( $L = \text{R-az}$  and  $\text{R-sb}$ ) complexes, is even more pronounced in the case of  $\text{cis-}[\text{Co}(\text{HL})_2\text{X}_2]$  complexes. The azo-ligands only form these complexes when R is an electron-donor substituent ( $\text{R} = 4'\text{-OMe}$  or  $4'\text{-Me}$ ). Azomethine ligands having a wide range of electron-donor and electron-acceptor substituents in the 4'-position form  $\text{cis-}[\text{Co}(\text{R-Hsb})_2\text{X}_2]$  complexes, and even when R is a sterically demanding group ( $-\text{CHMe}_2$ ) in the 2'-position it is possible to isolate the octahedral *cis* dihalogeno-complex. These differences serve to underline the importance of the advantage of non-planarity for the azomethine ligands which allows the 2'-substituent to avoid an unfavourable environment for chelation.

Although both series ( $\text{R-Haz}$  and  $\text{R-Hsb}$ ) of ligands give high-spin tetrahedral complexes,  $[\text{CoL}_2]$ , spectroscopic studies indicate that, whereas the ligand is bound in its keto-form [hydrazone, (1B)] when L is  $\text{R-az}$ , it is bound in the enol [enolimine, (2A)] form when L is  $\text{R-sb}$ .

The ease with which  $[\text{Co}(\text{R-Haz})_2\text{X}_2]$  and  $[\text{Co}(\text{R-az})_2]$  complexes can be oxidised to  $\text{fac-}[\text{Co}(\text{R-az})_3]$  is in marked contrast to the greater difficulty which is experienced in oxidising the analogous azomethine systems to give  $\text{fac-}[\text{Co}(\text{R-sb})_3]$  which are readily reduced to  $[\text{Co}(\text{R-sb})_2]$ . The complexes  $[\text{CoL}_2]$  and  $[\text{Co}(\text{HL})_2\text{X}_2]$  ( $L = \text{R-az}$  and  $\text{R-sb}$ ) are readily interconverted with acid and base. In both cases, the protonation requires slow addition of HX to  $[\text{CoL}_2]$  if  $[\text{Co}(\text{HL})_2\text{X}_2]$  is to be formed in high yield. The reaction with base is a rapid and clean reaction when it is carried out anaerobically, but when air is present in the reaction of  $[\text{Co}(\text{R-Haz})_2\text{X}_2]$  with base, oxidation occurs to give  $\text{fac-}[\text{Co}(\text{R-az})_3]$ . The corresponding acid-catalysed oxidation does not occur in the case of  $\text{cis-}[\text{Co}(\text{R-Hsb})_2\text{X}_2]$ . Reaction between equimolar proportions of  $[\text{Co}(\text{HL})_2\text{X}_2]$  and base produces five-co-ordinate  $[\text{Co}(\text{HL})(\text{L})\text{X}]$  ( $L = \text{R-sb}$ ,  $\text{R} = 4'\text{-OMe}$ ,  $4'\text{-Me}$ , or  $\text{H}$ ), but either oxidation {to  $[\text{CoL}_3]$  ( $L =$

$\text{R-az}$ )} or complete dehydrohalogenation {to  $[\text{CoL}_2]$  ( $L = \text{R-sb}$ )} is observed in all the other systems investigated under the same conditions.

It is clear that the isoelectronic ligands  $\text{R-Haz}$  and  $\text{R-Hsb}$  should *not* be regarded as closely comparable, still less as identical in their reactivity towards cobalt(II). Co-ordination to the metal probably starts from the more abundant keto-tautomer [(1B), (2B)] in each case by formation of a bond to nitrogen; intramolecular rotation of the unidentate ligand precedes chelation which is followed by loss of a proton. The ability of the ligand to become non-planar as a result of rotation about the phenyl(C)-N bond plays a crucial role in promoting the stability of the different complexes by diminishing unfavourable non-bonding steric interactions.

#### EXPERIMENTAL

All reactions requiring an inert atmosphere were carried out in dry, deoxygenated dinitrogen using conventional vacuum-line and Schlenk-tube techniques. Solvents were dried, deaerated, and distilled before use. Melting points were recorded on a calibrated hot-stage block. Infrared spectra were recorded as mulls (Nujol, hexachlorobutadiene) on PE 257 (NaCl plates) or 457 (CsI plates) grating infrared spectrometers in the range 200–4 000  $\text{cm}^{-1}$ , and calibrated with polystyrene. Electronic spectra were recorded with a PE 402 u.v.-visible spectrometer in a variety of solvents and diffuse reflectance spectra were measured with a Unicam SP700 instrument. Proton n.m.r. spectra were recorded on a PE R12B (60 MHz) spectrometer and <sup>13</sup>C n.m.r. spectra were recorded on a WP80 (20 MHz) spectrometer using  $\text{CDCl}_3$  as solvent. Magnetic measurements were performed by the Gouy method using a tube calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$ . Conductivity measurements were made on  $10^{-3}$  mol  $\text{dm}^{-3}$  solutions in various solvents using a Phillips PR 9500 conductivity bridge. The samples of cobalt(II) acetate and cobalt(II) halides were of reagent grade. The anhydrous cobalt(II) halides were prepared by heating the hydrated material at 120–140 °C under vacuum for 3–4 h. 4-Trifluoromethylaniline was obtained from Koch Light Laboratories. 2-Cyano- and 4-Cyano-aniline were provided by I.C.I. Organics Division. 2-(1-Methylethyl)aniline was purchased from Fluorchem Ltd. All other aromatic amines used were of reagent grade from B.D.H. Ltd., as was 2-hydroxy-1-naphthaldehyde. Azomethine ligands were prepared by heating equimolar quantities of 2-hydroxy-1-naphthaldehyde and the aromatic amine in ethanol at reflux for 20 min. The product crystallised from the reaction mixture on cooling to ambient temperature. The following compounds are reported for the first time. (a) 1-[(4'-Trifluoromethylphenylimino)methyl]-2-naphthol. Yellow crystals, m.p. 137–139 °C (Found: C, 68.8; H, 4.0; F, 17.6; N, 4.5. Calc. for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{NO}$ : C, 68.6; H, 3.8; F, 18.1; N, 4.4%).  $R_F$  (toluene) 0.40. <sup>1</sup>H N.m.r.  $\delta$  (p.p.m.) 6.92, 7.07 (d, H<sup>3</sup>), 7.63, 7.78 (d, H<sup>4</sup>), 8.00 (d, H<sup>8</sup>), 9.18 [C(11)H], 14.93 (OH/NH). (b) 1-[(4'-Cyano-phenylimino)methyl]-2-naphthol. Orange crystals, m.p. 232–234 °C (Found: C, 79.1; H, 4.3; N, 10.0. Calc. for  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}$ : C, 79.4; H, 4.4; N, 10.3%).  $R_F$  (toluene) 0.14. <sup>1</sup>H N.m.r.  $\delta$  (p.p.m.) 7.03, 7.18 (d, H<sup>3</sup>), 7.77, 7.92 (d, H<sup>4</sup>), 8.10 (d, H<sup>8</sup>), 9.34 [C(11)H], 14.80 (OH/NH). (c) 1-[[2'-(1-Methylethyl)phenylimino)methyl]-2-naphthol. Bright yellow crystals, m.p. 134–135 °C (Found: C, 82.2; H, 6.5; N,

4.6. Calc. for  $C_{20}H_{19}NO$ : C, 83.0; H, 6.6; N, 4.8%.  $R_F$  (toluene) 0.36.  $^1H$  N.m.r.  $\delta$  (p.p.m.) 1.30 (d,  $CH_3$ ), 3.45 (quintet, CH), 6.98, 7.14 (d,  $H^3$ ), 7.67, 7.83 (d,  $H^4$ ), 8.06 (d,  $H^8$ ), 9.22 [C(11)H], 15.55 (OH/NH). (d) 1-[(2'-Cyanophenylimino)methyl]-2-naphthol. Yellow crystals, m.p. 198 °C (Found: C, 79.0; H, 4.2; N, 10.1. Calc. for  $C_{18}H_{12}N_2O$ : C, 79.4; H, 4.4; N, 10.3%).  $R_F$  (toluene) 0.19.  $^1H$  N.m.r.  $\delta$  (p.p.m.) 7.03, 7.18 (d,  $H^3$ ), 7.72, 7.87 (d,  $H^4$ ), 8.08 (d,  $H^8$ ), 9.46 [C(11)H], 14.37 (OH/NH).

**Preparation of Bis{1-[(4'-substituted phenylimino)methyl]-2-naphtholato}cobalt(II) Complexes,  $[Co(R-sb)_2]$  ( $R = 4'-OMe, Me, Cl, Br, CF_3, CN, \text{ or } NO_2$ ).**—A solution of cobalt(II) acetate,  $Co[O_2CCH_3]_2 \cdot 4H_2O$  (0.01 mol), in methanol (15  $cm^3$ ) was added dropwise during 0.25 h to a stirred, refluxing mixture of the ligand R-Hsb (0.02 mol) in methanol (50  $cm^3$ ). The mixture was boiled under reflux for 1–2 h during which time a red microcrystalline solid was deposited from the solution. This red solid was isolated by filtration of the hot mixture, washed with methanol, and dried under vacuum. Analytical and representative physical and spectroscopic data <sup>6</sup> for these complexes are collected in Table 3.

**Preparation of Bis{1-[(2'-substituted phenylimino)methyl]-2-naphtholato}cobalt(II) Complexes,  $[Co(R-sb)_2]$  ( $R = 2'-OMe, CHMe_2, \text{ or } Cl$ ).**—A solution of cobalt(II) acetate,  $Co[O_2CCH_3]_2 \cdot 4H_2O$  (0.01 mol), in nitrogen-purged, dry methanol (15  $cm^3$ ) was added dropwise during 0.25 h to a stirred, refluxing mixture of the ligand, R-Hsb (0.02 mol), in nitrogen-purged dry methanol (50  $cm^3$ ). The mixture was boiled under reflux in a nitrogen atmosphere for 24 h, during which time a red microcrystalline solid was deposited from the solution. This red solid was isolated by filtration under anaerobic conditions of the hot reaction mixture. The solid was then washed with nitrogen-purged dry methanol and dried under vacuum. Analytical and representative physical and spectroscopic <sup>6</sup> data for these complexes are collected in Table 3.

**Preparation of cis-Dihalogenobis{1-[(4'-substituted phenylimino)methyl]-2-naphtholato}cobalt(II) Complexes, cis- $[Co(R-Hsb)_2X_2]$  ( $R = H, 4'-OMe, 4'-Me, 4'-Cl, \text{ or } 4'-Br$ ).**—A solution of the anhydrous cobalt(II) halide,  $CoX_2$  ( $X = Cl \text{ or } Br$ ) (0.005 mol), in dry ethanol (15  $cm^3$ ) was added dropwise during 0.25 h to a stirred refluxing solution of the ligand, R-Hsb (0.01 mol), in dry ethanol (100  $cm^3$ ). The dark green mixture was heated under reflux for 24 h, during which time a dark green solid was deposited from the solution. The dark green solid was isolated by filtration of the hot reaction mixture, washed with dry ethanol, and dried under vacuum. The dry solid was then subjected to Soxhlet extraction with ethanol for 8 h giving one product only as dark green crystals. Analytical and representative physical and spectroscopic <sup>6</sup> data for these complexes are collected in Table 4.

**Preparation of cis-Dihalogenobis{1-[(R-phenylimino)methyl]-2-naphtholato}cobalt(II) Complexes, cis- $[Co(R-Hsb)_2X_2]$  ( $R = 4'-CF_3, 2'-CHMe_2, \text{ or } 2'-Me$ ).**—A solution of the anhydrous cobalt(II) halide  $CoX_2$  ( $X = Cl \text{ or } Br$ ) (0.002 mol) in deaerated dry ethanol (15  $cm^3$ ) was added dropwise during 0.25 h to a stirred refluxing solution of the ligand, R-Hsb (0.004 mol), in deaerated dry ethanol (75  $cm^3$ ) under nitrogen. The dark green solid which was deposited from the refluxing solution during a period of 24 h was isolated by filtration of the hot reaction mixture under anaerobic conditions, washed with deaerated dry ethanol, and dried under vacuum. Analytical and representative physical and

spectroscopic <sup>6</sup> data for the green crystalline complexes are collected in Table 4.

**Reaction of  $[Co(R-sb)_2]$  ( $R = H$ ) with Hydrochloric Acid.**—Hydrochloric acid (1.0  $cm^3$  of 10 mol  $dm^{-3}$  solution, 0.01 mol) was added dropwise during 0.25 h to a stirred refluxing mixture of  $[Co(R-sb)_2]$  ( $R = H, 2.75 \text{ g, } 0.005 \text{ mol}$ ) in dry ethanol (100  $cm^3$ ). The colour of the reaction mixture changed from red to green on addition of the acid. The mixture was heated under reflux during 1 h, allowed to cool slightly, concentrated (to 50  $cm^3$ ), and then filtered. A green solid was isolated, washed with ethanol, and dried (Found: C, 65.0; H, 4.0; Cl, 10.0; Co, 8.9; N, 4.3. Calc. for  $C_{34}H_{26}ClCoN_2O_2$ : C, 65.4; H, 4.2; Cl, 11.3; Co, 9.3; N, 4.5%).

**Reaction of cis- $[Co(R-Hsb)_2X_2]$  ( $R = H, 4'-OMe, 4'-Me, \text{ or } 4'-Cl; X = Cl \text{ or } Br$ ) with Potassium Acetate.**—(a) A filtered solution of potassium acetate (0.008 mol) in ethanol (15  $cm^3$ ) was added to a stirred, refluxing mixture of the green cobalt(II) complex,  $[Co(R-Hsb)_2X_2]$  (0.004 mol), in ethanol (50  $cm^3$ ). The mixture was heated at reflux for 0.5 h during which time a red crystalline product was deposited from the solution. The red solid was isolated by filtration and washed successively with ethanol (2  $\times$  10  $cm^3$ ), then water until the washings were halide-free, and again with ethanol (20  $cm^3$ ). The solid was dried under vacuum [( $R = H$ ), Found: C, 73.9; H, 4.4; Co, 10.5; N, 5.1. Calc. for  $C_{34}H_{24}CoN_2O_2$ : C, 74.1; H, 4.4; Co, 10.7; N, 5.1%]. [( $R = 4'-OMe$ ), Found: C, 69.1; H, 4.3; Co, 9.5; N, 4.4. Calc. for  $C_{36}H_{28}CoN_2O_4$ : C, 70.7; H, 4.6; Co, 9.6; N, 4.6%]. [( $R = 4'-Me$ ), Found: C, 74.9; H, 4.9; Co, 10.6; N, 4.8. Calc. for  $C_{36}H_{28}CoN_2O_2$ : C, 74.6; H, 4.8; Co, 10.2; N, 4.8%]. [( $R = 4'-Cl$ ), Found: C, 65.6; H, 3.4; Cl, 11.0; Co, 9.8; N, 4.4. Calc. for  $C_{34}H_{22}Cl_2CoN_2O_2$ : C, 65.8; H, 3.6; Cl, 11.5; Co, 9.5; N, 4.5%].

(b) A filtered solution of potassium acetate (0.001 mol) in dry ethanol (5  $cm^3$ ) was added dropwise during 0.25 h to a stirred, refluxing solution of the green cobalt(II) complex  $[Co(R-Hsb)_2X_2]$  (0.001 mol) in the minimum quantity of dry ethanol required to dissolve the complex. After about 0.25 h, a yellow-brown precipitate started to form. It was occasionally necessary to add a small quantity of fresh solvent in order to assist stirring. The yellow-brown precipitate slowly redissolved. The reaction mixture was heated at reflux for a total of 15 h during which dark purple crystals were deposited from the solution. The purple solid was isolated by filtration, washed with dry ethanol, then with water until the washings were halide-free, then with ethanol again. The solid product was dried under vacuum [( $R = 4'-OMe; X = Cl$ ), Found: C, 67.2; H, 4.4; Cl, 5.5; Co, 9.4; N, 4.3. Calc. for  $C_{36}H_{29}ClCoN_2O_4$ : C, 66.7; H, 4.5; Cl, 5.5; Co, 9.1; N, 4.3%]. [( $R = 4'-OMe; X = Br$ ), Found: C, 62.2; H, 4.2; Br, 11.6; Co, 8.6; N, 4.0. Calc. for  $C_{36}H_{29}BrCoN_2O_4$ : C, 62.4; H, 4.2; Br, 11.5; Co, 8.5; N, 4.0%]. [( $R = 4'-Me; X = Cl$ ), Found: C, 69.8; H, 4.7; Cl, 5.4; Co, 9.4; N, 4.8. Calc. for  $C_{36}H_{29}ClCoN_2O_2$ : C, 70.2; H, 4.8; Cl, 5.8; Co, 9.6; N, 4.5%]. [( $R = 4'-Me; X = Br$ ), Found: C, 65.6; H, 4.4; Br, 12.1; Co, 9.2; N, 4.2. Calc. for  $C_{36}H_{29}BrCoN_2O_2$ : C, 65.5; H, 4.4; Br, 12.1; Co, 8.9; N, 4.2%]. Infrared spectra of  $[Co(R-sb)(R-Hsb)X]$  (200–400  $cm^{-1}$  region only): ( $R = 4'-OMe; X = Cl$ ) 385w, 347m, 317s, 295m, 270w br, and 250w  $cm^{-1}$ . ( $R = 4'-OMe; X = Br$ ) 390w, 345w, 325w, 295m, 280m, and 240s  $cm^{-1}$ . ( $R = 4'-Me; X = Cl$ ) 380w, 350m, 338w, 313s, and 270m  $cm^{-1}$ . ( $R = 4'-Me, X = Br$ ) 380w, 350m, 338w, 300w, 271m, and 240s  $cm^{-1}$ .

*Preparation of fac-[Tris{2-[(4'-methylphenylimino)methyl]-naphtholato}cobalt(III)].*—A solution of cobalt(II) acetate (1.24 g, 0.005 mol) in methanol (10 cm<sup>3</sup>) was added dropwise during 0.25 h to a stirred refluxing solution of the ligand 1-[(4'-methylphenylimino)methyl]-2-naphthol (4.0 g, 0.015 mol) in methanol (150 cm<sup>3</sup>). Hydrogen peroxide (10 cm<sup>3</sup>, 100 vol.%) was added and the resulting mixture was heated at reflux for 2 h, during which time the colour of the mixture changed from red to green and a green crystalline solid was deposited. The green solid was isolated by filtration of the hot mixture, washed with methanol, and dried under vacuum (Found: C, 77.0; H, 4.8; Co, 6.7; N, 5.1. Calc. for C<sub>54</sub>H<sub>42</sub>CoN<sub>3</sub>O<sub>3</sub>: C, 77.2; H, 5.0; Co, 7.0; N, 5.0%). <sup>1</sup>H N.m.r. δ (p.p.m.) 1.70 (s, 3 H), 2.05 (s, 3 H), 2.20 (s, 3 H), 6.0–8.5 (m, 33 H).

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