Electron Spin Resonance Spectra of Five- and Six-Co-ordinate Cobalt(II)–Methyl Isocyanide Complexes in Co^{II}Y Zeolites

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Summary The penta- and hexa-co-ordinate low-spin cobalt(II)–methyl isocyanide complexes were formed in the Co^{II}Y zeolites.

An attempt to synthesize well defined transition-metal complexes within a dehydrated zeolite framework has led to the present work on cobalt(II) methyl isocyanide complexes. Such zeolite–transition-metal complexes are potentially the heterogeneous analogues of important homogeneous catalysts.

Recently, there has been considerable interest in low-spin alkyl and aryl isonitrile cobalt(II) complexes in frozen solutions and salts.[1–5] The most stable complexes are the five-co-ordinate complexes, however, a six-co-ordinate complex has been reported in the presence of an excess of the ligand. These low-spin cobalt(II) complexes have essentially a C_{4v} or square pyramidal symmetry with the unpaired electron in the d_{z^2} orbital.

In order to form complexes and lower the spin state of the exchangeable Co^{2+} ions in the zeolite cavities, methyl isocyanide was adsorbed at room temperature in a Co^{II}Y zeolite which had been degassed at 500 °C. The methyl isocyanide adsorbed rapidly in the zeolite with the concomitant formation of the complexes. The X and Q band spectra, recorded at −196 °C, of the Co^{II}–CH_3NC complexes in the Co^{II}Y zeolite are shown in the Figure.

The spectrum, shown in the Figure (a), is attributed to the presence of $Co(CH_3NC)_5^{2+}$ ions in the supercages of the zeolite. Indeed, the ^{59}Co hyperfine interactions produce two sets of eight lines corresponding to the parallel and perpendicular directions of the symmetry axis with respect to the external magnetic field. In the presence of an excess of CH_3NC the X band spectrum, as shown in (b), becomes more isotopic. This indicates that the cobalt(II)-methyl isocyanide complex in the zeolite cavities must be essentially hexa-co-ordinated. The Q band spectrum, however, accentuates the anisotropic behaviour of the Co^{II} complex, and suggests unequal bond distances. The e.s.r. parameters for the penta- and hexa-co-ordinate methyl isocyanide complexes of cobalt(II)Y zeolites are summarized in the Table.

TABLE. *E.s.r. parameters for penta- and hexa-co-ordinated methyl isocyanide complexes of cobalt*(II) *in* $Co^{II}Y$ *zeolites*

Complexes	Band	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}$	$a_{\perp}$	$\frac{\lambda}{\Delta}$	κ	a_{iso}	2B
$Co(CH_3NC)_5^{2+}$	X	2·003 ±0·002	2·172 ±0·004	89G ±1	−32G ±1	0·0282	0·093	−12·7G	106·2G
$Co(CH_3NC)_6^{2+}$	X	2·008 ±0·002	2·087 ±0·004	68G ±1	−72G ±1	0·0141	0·187	−35·9G	105·8G
	Q	2·006 ±0·002	2·084 ±0·004	66G ±2	−73G ±2	0·0136	0·189	−36·5G	104·6G

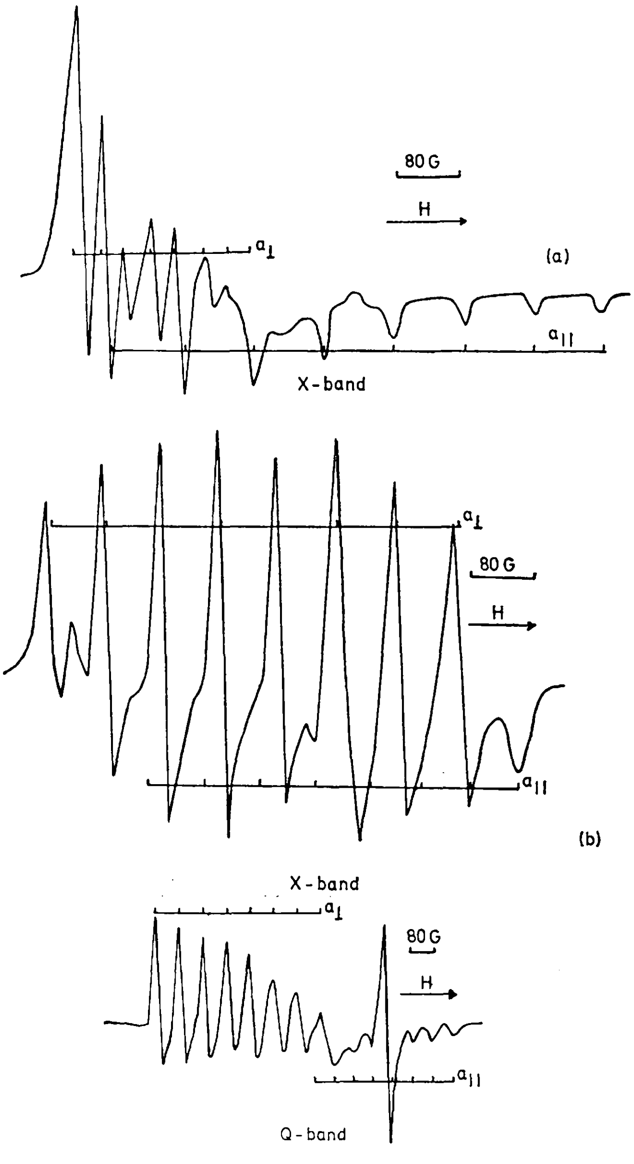

FIGURE. *E.s.r. spectra of cobalt*(II)*-methyl isocyanide complexes:* (*a*) $Co(CH_3NC)_5^{2+}$; (*b*) $Co(CH_3NC)_6^{2+}$. *The symmetric line in the Q-band spectrum at the centre of* $a_{\parallel}$ *is due to another species.*

The experimental e.s.r. parameters are consistent with those observed in other matrices so that a C_{4v} symmetry of the complexes may be assumed; therefore, the expected ground-state can be expressed as $(d_{xz,yz})^4(d_{xy})^2\ (d_{z^2})$.[1] For the unpaired electron in the d_{z^2} orbital, the principal values of the g tensor are given by equation (1)[6] where $g_e = 2{\cdot}0023$,

$$g_{\parallel} = g_e \text{ and } g_{\perp} = g_e + 6\frac{\lambda}{\Delta} \qquad (1)$$

λ is the spin-orbit parameter, and Δ the energy between the $d_{xz,yz}$ and the d_{z^2} orbitals.

The hyperfine coupling constant and their ratio for the low-spin d^7 cobalt ion in a C_{4v} symmetry can be given approximately by equations (2) and (3),

$$a_{\perp} = a_{iso} - B(1 - \frac{45}{12}\Delta g_{\perp});a_{\parallel} = a_{iso} + 2B(1 - \frac{\Delta g_{\perp}}{4}) \qquad (2)$$

and

$$\frac{a_{\parallel}}{a_{\perp}} = \frac{(-\kappa + 4/7 - \frac{6\lambda}{7\Delta})}{(-\kappa - 2/7 + \frac{45\lambda}{7\Delta})} \qquad (3)$$

where κ is associated with the ligand-field mixing of the $3d^64s$ into the $3d^7$ state, a_{iso} and 2B are the isotropic and anisotropic hyperfine parameters in the absence of orbital magnetism, and $\Delta g_{\perp} = g_{\perp} - g_e$. The Table shows the values of k, λ/Δ, a_{iso}, and 2B for the penta- and hexa-co-ordinate cobalt(II) complexes. The value of a_{iso} for $Co(CH_3NC)_5^{2+}$ confirms that the complex is only weakly co-ordinated to the zeolite framework.[2] When the unpaired electron is in the d_{z^2} orbital, the hyperfine coupling constants have the following signs: $a_{\parallel} > 0$, $a_{\perp} < 0$, $a_{iso} < 0$ and $2B > 0$.[2] The κ values indicated that the mixing of the $3d$ and $4s$ orbital of the cobalt in the six-co-ordinate isonitrile complex is much less than in the penta-co-ordinate complex. Using equation (4),[2] the spin density in the $4s$

$$a_{iso} = x\ a_{iso}(4s) + (1 - x)a_{iso}\ (3d, \text{ spin-polarization}) \qquad (4)$$

orbital (x) can be calculated. Our results give a spin density in the $4s$ orbital of 3·8% and 5·4% for the six- and five-co-ordinate methyl isocyanide complexes in the $Co^{II}Y$ zeolites.

Generally, we may conclude, bivalent cobalt ions move out into the large cavities to form penta- and hexa-coordinate cobalt(II)-methyl isocyanide complexes which are essentially the same as those observed in other media. The work presented here represents one of the few successful attempts to produce well characterized transition-metal complexes within a zeolite framework. The square planar $Cu(NH_3)_4^{2+}$ and $Cu(pyridine)_4^{2+}$ complexes in zeolites have also been recently reported.[7,8]

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