*In memory of S. M. Nelson*

# Complexes of Cobalt(II) and Nickel(II) with 3- and 4-Acetylpyridine

**M. Fermamda Cabral and João de O. Cabral** *
*Laboratório Ferreira da Silva, Faculdade de Ciências, 4000 Porto, Portugal*

Fifteen complexes of cobalt(II) and nickel(II) with 3- and 4-acetylpyridine, 10 of the general formula $[MX_2L_n]$ (M = Co or Ni; X = Cl, Br, I, or NCS; L = 3-acetylpyridine; *n* = 2 or 4), and five of the general formula $[CoX_2L_2]$ (X = Cl, Br, I, or NCS; L = 4-acetylpyridine), have been prepared, 13 of them for the first time. From the results of chemical analysis, magnetic susceptibility measurements, electronic and i.r. spectra, several structural types are postulated: pseudo-tetrahedral, monomeric; pseudo-octahedral, monomeric; and pseudo-octahedral, polymeric.

Monoacetylpyridines possess two potential donor atoms, the heterocyclic nitrogen and the carbonyl oxygen, which might allow them to behave either as bidentate or ambidentate ligands.

Of the three isomers, only 2-acetylpyridine has the co-ordinating ability to form chelates, *e.g.* with cobalt(II) and nickel(II), among other metal ions.[1]

Studies on complexes of cobalt(II) and nickel(II) with 3- and 4-acetylpyridine (3-acpy and 4-acpy) are remarkably absent. Only two cobalt(II) complexes, $[CoCl_2(4\text{-acpy})_2]$[2] and '$Co(NCS)_2(4\text{-acpy})_2\cdot 2H_2O$,'[3] not well characterized, seem to have been reported, and no mention of isolated 3-acetylpyridine complexes of $Co^{II}$ or $Ni^{II}$ has been found.

In view of the biological importance of 3-acetylpyridine and, to a lesser extent, of 4-acetylpyridine, the study of their complexes with such essential metal ions as $Co^{II}$ and $Ni^{II}$ was of interest.

In this paper we describe the synthesis and properties of a series of complexes of $Co^{II}$ and $Ni^{II}$ with 3-acetylpyridine and of $Co^{II}$ with 4-acetylpyridine. From these properties, possible structures for the complexes are suggested. A previously prepared complex, $[Co(NCS)_2(4\text{-acpy})_2(H_2O)_2]$, has since been studied by *X*-ray crystallography, and its crystal structure reported.[4]

## Results and Discussion

The synthesis of the complexes is described in the Experimental section. Chemicals of the highest commercially available quality were used throughout, without any further purification.

*Characterization.*—The complexes studied are listed in Table 1 along with analytical and other data. The analytical results are generally in very good agreement with the required values, taking into account the presence of water in four of the complexes [(**6**), (**7**), (**10**), and (**15**)]. It will be shown that in (**6**), (**10**), and (**15**) the water molecules are co-ordinated to the metal ion, but not in (**7**). If for the $Co^{II}$ complexes the values of magnetic moments provide a clear-cut distinction between four-and six-co-ordination, the same is not applicable to the $Ni^{II}$ complexes.[5] The very low solubility of (**7**) and (**8**) in nitromethane, acetone, and chloroform was considered as evidence for their polymeric nature.[6]

*Electronic Spectra.*—Since most of the complexes were either practically insoluble in all common solvents or decomposed by them, only diffuse reflectance spectra could be obtained for all of them; the characteristics of these spectra are summarized in Table 2.

The assignment of band positions was based on Lever's criteria,[7] the experimental values being consistent with the following configurations: (*i*) complexes (**1**), (**2**), (**7**), (**8**), (**11**), (**12**), and (**14**) must be six-co-ordinate, pseudo-octahedral, with a highly distorted $O_h$ configuration, because of their polymeric nature; (*ii*) (**3**) and (**13**) must be pseudo-tetrahedral; and (*iii*) (**4**), (**5**), (**6**), (**9**), (**10**), and (**15**) can only be pseudo-octahedral and monomeric.

From these results it can be concluded that 3- and 4-acetylpyridine act as monodentate ligands in the 15 complexes prepared, either through the heterocyclic nitrogen atom or the carbonyl oxygen atom, the first hypothesis being the most reasonable.

*Infrared Spectra.*—Katritzky *et al.* described and discussed 11 characteristic bands for 3-acetylpyridine[8] and eight for 4-acetylpyridine.[9] Hence the i.r. spectra of the complexes were rather complex, and it was necessary to select a limited number of bands which were considered more significant (Table 3). These bands were: (*i*) the stretching vibration of the carbonyl group, ν(CO), which is considered very sensitive to co-ordination of the oxygen atom;[10—13] (*ii*) pyridine ring vibrations more sensitive to co-ordination of the heterocyclic nitrogen atom, which some authors[10,14,15] consider to be ν(8a), and some others[16,17] to be ν(12); (*iii*) the three fundamental vibrations of $SCN^-$, which can provide some information on the co-ordination mode of this anion.[18]

For free 3-acetylpyridine the following values were found: ν(CO) at 1 675, ν(8a) at 1 590, and ν(12) at 1 020 $cm^{-1}$. For 4-acetylpyridine, the values were: ν(CO) at 1 690, ν(8a) at 1 590, and ν(12) at 1 020 $cm^{-1}$. In the 10 3-acetylpyridine complexes the values for ν(CO) were found in the region 1 695—1 670 $cm^{-1}$, and in the five 4-acetylpyridine complexes, 1 698—1 675 $cm^{-1}$. It can, therefore, be assumed that the CO groups of both 3-and 4-acetylpyridine are not co-ordinated.

For the ν(8a) band, values were found in the region 1 595—1 568 $cm^{-1}$ for the 3-acetylpyridine complexes, and 1 635—1 605 $cm^{-1}$ for the 4-acetylpyridine complexes. The ν(12) band appeared at 1 050—1 020 $cm^{-1}$ for the 3-acetylpyridine complexes, and at 1 018—1 015 $cm^{-1}$ for the 4-acetylpyridine complexes.

According to Goher and Attia,[17] on complexation the ν(8a) band of 3-acetylpyridine is displaced 10—15 $cm^{-1}$, and ν(12) displaced 15—20 $cm^{-1}$, both to higher wavenumbers. Wong and Brewer[16] consider that the ν(12) mode of 4-acetylpyridine is

**Table 1.** Analytical[a] data and other characteristic properties

| Complex | Colour | Analysis (%) M | X | C | H | N | $\mu_{eff.}$[b] |
|---|---|---|---|---|---|---|---|
| **(1)** $[\{CoCl_2(3\text{-acpy})_2\}_n]$ | Lilac-blue | 15.9 | 19.0 | — | — | — | 5.37 |
| | | (15.8) | (19.1) | | | | |
| **(2)** $[\{CoBr_2(3\text{-acpy})_2\}_n]$ | Lilac | 12.7 | 34.6 | — | — | — | 5.30 |
| | | (12.8) | (34.7) | — | — | — | |
| **(3)** $[CoI_2(3\text{-acpy})_2]$ | Green | 10.4 | 44.9 | | | | 4.72 |
| | | (10.6) | (45.7) | — | — | — | |
| **(4)** $[CoI_2(3\text{-acpy})_4]$ | Brownish red | 7.4 | 32.1 | 41.9 | 3.6 | 6.5 | 5.18 |
| | | (7.4) | (31.8) | (42.2) | (3.5) | (7.0) | |
| **(5)** $[Co(NCS)_2(3\text{-acpy})_4]$ | Bluish purple | 8.8 | 17.7 | 54.8 | 4.3 | 12.5 | 5.11 |
| | | (8.9) | (17.6) | (54.6) | (4.3) | (12.8) | |
| **(6)** $[Co(NCS)_2(3\text{-acpy})_2(H_2O)_2]$ | Brick red | 13.0 | 25.3 | 42.8 | 4.2 | 11.7 | 5.06 |
| | | (13.0) | (25.6) | (42.4) | (4.0) | (12.4) | |
| **(7)** $[\{NiCl_2(3\text{-acpy})_2\}_n]\cdot mH_2O$ | Greenish yellow | 15.1 | 18.2 | — | — | — | 3.34 |
| | | (15.1) | (18.2) | — | — | — | |
| **(8)** $[\{NiBr_2(3\text{-acpy})_2\}_n]$ | Yellowish green | 12.8 | 34.6 | — | — | — | 3.41 |
| | | (12.8) | (34.7) | — | — | — | |
| **(9)** $[Ni(NCS)_2(3\text{-acpy})_4]$ | Lilac-blue | 8.9 | 17.7 | 53.9 | 4.5 | 12.4 | 3.30 |
| | | (8.9) | (17.6) | (54.6) | (4.3) | (12.8) | |
| **(10)** $[Ni(NCS)_2(3\text{-acpy})_2(H_2O)_2]$ | Turquoise-blue | 12.7 | 25.2 | 42.8 | 4.2 | 12.1 | 3.20 |
| | | (13.0) | (25.6) | (42.4) | (4.0) | (12.4) | |
| **(11)** $[\{CoCl_2(4\text{-acpy})_2\}_n]$ | Bluish lilac | 15.9 | 19.4 | — | — | — | 5.37 |
| | | (15.8) | (19.1) | — | — | — | |
| **(12)** $[\{CoBr_2(4\text{-acpy})_2\}_n]$ | Pink-lilac | 12.5 | 34.7 | — | — | — | 5.24 |
| | | (12.8) | (34.7) | — | — | — | |
| **(13)** $[CoI_2(4\text{-acpy})_2]$ | Green | 10.5 | 44.5 | — | — | — | 4.52 |
| | | (10.6) | (45.7) | — | — | — | |
| **(14)** $[\{Co(NCS)_2(4\text{-acpy})_2\}_n]$ | Bluish pink | 14.1 | 27.7 | — | — | — | 5.05 |
| | | (14.1) | (27.8) | — | — | — | |
| **(15)** $[Co(NCS)_2(4\text{-acpy})_2(H_2O)_2]$ | Orange | 13.1 | 25.2 | — | — | — | 5.15 |
| | | (13.0) | (25.6) | — | — | — | |

[a] Required values are given in parentheses. [b] Measured at 25 °C; corrected for diamagnetism of ligands.

**Table 2.** Electronic spectra of the $Co^{II}$ and $Ni^{II}$ complexes

| Complex | Band position*/cm$^{-1}$ $10^{-3}\nu_1$ | $10^{-3}\nu_2$ | $10^{-3}\nu_3$ |
|---|---|---|---|
| **(1)** $[\{CoCl_2(3\text{-acpy})_2\}_n]$ | 8.50 (s), 5.80 (s) | | 20.20 (sh), 18.80 (vs), 17.60 (s), 16.10 (s) |
| **(2)** $[\{CoBr_2(3\text{-acpy})_2\}_n]$ | 8.20 (s), 5.80 (s) | | 19.70 (sh), 18.40 (vs), 17.30 (sh), 15.40 (s) |
| **(3)** $[CoI_2(3\text{-acpy})_2]$ | | 9.00 (s), 6.80 (s), 5.70 (sh) | 19.80 (w), 16.20 (sh), 15.20 (vs) |
| **(4)** $[CoI_2(3\text{-acpy})_4]$ | 8.40 (s), 6.10 (s) | | 20.00 (vw), 18.40 (w), 17.80 (w), 16.70 (sh) |
| **(5)** $[Co(NCS)_2(3\text{-acpy})_4]$ | 9.40 (s) | | 21.20 (s), 20.00 (s), 18.00 (sh), 16.00 (sh) |
| **(6)** $[Co(NCS)_2(3\text{-acpy})_2(H_2O)_2]$ | 8.70 (s), 7.20 (sh) | | 21.40 (s), 19.40 (s) |
| **(7)** $[\{NiCl_2(3\text{-acpy})_2\}_n]\cdot mH_2O$ | 8.40 (s), 6.20 (s) | 14.50 (s), 12.40 (w) | 23.6 (c.t.?), 22.5 (c.t.?) |
| **(8)** $[\{NiBr_2(3\text{-acpy})_2\}_n]$ | 8.00 (s), 5.80 (s) | 13.60 (s), 11.70 (sh) | 22.3 (c.t.?), 21.4 (sh) |
| **(9)** $[Ni(NCS)_2(3\text{-acpy})_4]$ | 10.80 (s) | 17.40 (s) | |
| **(10)** $[Ni(NCS)_2(3\text{-acpy})_2(H_2O)_2]$ | 10.80 (s), 9.20 (s) | 16.60 (s) | 22.2 (c.t.?) |
| **(11)** $[\{CoCl_2(4\text{-acpy})_2\}_n]$ | 9.00 (w), 6.80 (w) | | 20.40 (sh), 19.00 (w), 18.00 (w), 16.30 (w) |
| **(12)** $[\{CoBr_2(4\text{-acpy})_2\}_n]$ | 8.40 (w), 6.10 (w), 5.80 (w) | | 20.20 (sh), 18.60 (w), 17.60 (sh), 15.60 (w) |
| **(13)** $[CoI_2(4\text{-acpy})_2]$ | | 9.60 (s), 7.40 (w), 7.00 (sh) | 19.70 (sh), 16.00 (sh), 14.80 (vs) |
| **(14)** $[\{Co(NCS)_2(4\text{-acpy})_2\}_n]$ | 10.00 (sh), 7.60 (w) | | 19.20 (s), 18.20 (s), 17.40 (sh) |
| **(15)** $[Co(NCS)_2(4\text{-acpy})_2(H_2O)_2]$ | 9.30 (s), 7.40 (sh) | | 19.20 (s), 18.40 (s), 17.40 (sh) |

* c.t. = Charge transfer.

shifted *ca.* 35 cm$^{-1}$ to higher values by complex formation with both copper(II) and zinc(II) ions. Our results do not entirely fit in with these findings. For the complexes with 3-acetylpyridine we observed a similar shift for the ν(12) mode, but not for ν(8a); with the complexes of 4-acetylpyridine we observed exactly the opposite kind of band maxima displacements. It can, therefore, be questioned which mode, ν(12) or ν(8a), is more sensitive to co-ordination through the pyridine nitrogen atom; this may well depend not only on the nature and position of the substituents on the pyridine ring but also on the metal ion of the complex.

Whatever mode is more sensitive to co-ordination, since in our complexes it is not the oxygen atom of the CO group which is co-ordinated and the pyridine ligands are unidentate, there seems to be no doubt that the heterocyclic nitrogen is the donor atom.

The experimental values found for the three fundamental vibration modes of $SCN^-$ are consistent with co-ordination

**Table 3.** Infrared spectral data for the $Co^{II}$ and $Ni^{II}$ complexes

| | $\nu_{max.}/cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Complex | ν(CO) | ν(8a) | ν(12) | ν(CN) | ν(CS) | δ(NCS) |
| **(1)** $[\{CoCl_2(3\text{-}acpy)_2\}_n]$ | 1 690s | 1 595s | 1 045m<br>1 030w | | | |
| **(2)** $[\{CoBr_2(3\text{-}acpy)_2\}_n]$ | 1 690s | 1 595s | 1 045m<br>1 030s | | | |
| **(3)** $[CoI_2(3\text{-}acpy)_2]$ | 1 685vs | 1 595m | 1 049m<br>1 035vw | | | |
| **(4)** $[CoI_2(3\text{-}acpy)_4]$ | 1 675vs | 1 586vs | 1 042s<br>1 030vw | | | |
| **(5)** $[Co(NCS)_2(3\text{-}acpy)_4]$ | 1 680vs | 1 590s<br>1 568m | 1 040s<br>1 033s | 2 050vs | 825s<br>695vs | 490vw<br>482vw |
| **(6)** $[Co(NCS)_2(3\text{-}acpy)_2(H_2O)_2]$ | 1 670vs | 1 590vs | 1 043w<br>1 030m | 2 080vs | 786m | 488m<br>470m |
| **(7)** $[\{NiCl_2(3\text{-}acpy)_2\}_n]\cdot mH_2O$ | 1 680vs | 1 595vs | 1 050s<br>1 030s | | | |
| **(8)** $[\{NiBr_2(3\text{-}acpy)_2\}_n]$ | 1 695m | 1 595w | 1 050s<br>1 030s | | | |
| **(9)** $[Ni(NCS)_2(3\text{-}acpy)_4]$ | 1 685vs | 1 595vs | 1 040s<br>1 030m | 2 080vs | 830m<br>818s<br>642s | 480w |
| **(10)** $[Ni(NCS)_2(3\text{-}acpy)_2(H_2O)_2]$ | 1 675vs | 1 590vs | 1 045s<br>1 030m<br>1 020w | 2 095vs | 790s<br>645s | 500m<br>480m<br>471m |
| **(11)** $[\{CoCl_2(4\text{-}acpy)_2\}_n]$ | 1 698vs | 1 605w | 1 015m | | | |
| **(12)** $[\{CoBr_2(4\text{-}acpy)_2\}_n]$ | 1 698vs | 1 605vw | 1 015m | | | |
| **(13)** $[CoI_2(4\text{-}acpy)_2]$ | 1 685s | 1 610m | 1 018w | | | |
| **(14)** $[\{Co(NCS)_2(4\text{-}acpy)_2\}_n]$ | 1 690s | 1 610vw | 1 016w | 2 120vs<br>2 105vs | 788w<br>760w | |
| **(15)** $[Co(NCS)_2(4\text{-}acpy)_2(H_2O)_2]$ | 1 675s | 1 635s | 1 016s | 2 090vs | 802m<br>760s | 475s |

through the nitrogen atom for complexes **(5)**, **(6)**, **(9)**, **(10)**, and **(15)**, and with thiocyanate bridges in the case of complex **(14)**.

In the i.r. spectra of complexes **(6)**, **(10)**, and **(15)** a strong, broad, band was observed at *ca.* 3 300 $cm^{-1}$, which was assigned to water co-ordinated to the metal ion. For complex **(7)**, three sharp, weak, bands were found in the region 3 350—3 050 $cm^{-1}$, probably due to unco-ordinated water. We have no experimentally substantiated evidence as to the nature and role of the water molecules in complex **(7)**, which may be clathrated, similar to the situation reported for analogous $Ni^{II}$ complexes,[19] or hydrogen bonded to the carbonyl group.

*Crystalline Molecular Structure.*—The *X*-ray determination of the molecular structure of $[Co(NCS)_2(4\text{-}acpy)_2(H_2O)_2]$ **(15)** has already been published.[4] It was shown that the $Co^{II}$ ion is bonded to two thiocyanate ligands (Co–N 2.080 Å), two 4-acetylpyridine ligands (Co–N 2.195 Å), and to two water molecules (Co–O 2.130 Å), in perfect agreement with the results reported here. This structure is quite similar to that described by Long *et al.*[20] for the analogous complex $[Fe(NCS)_2(4\text{-}acpy)_2(H_2O)_2]$, as was to be expected.

This determination proved that the structure suggested for $[Co(NCS)_2(4\text{-}acpy)_2(H_2O)_2]$, on the basis of other experimental data, was correct. As a consequence, we feel confident that the other 14 complexes, not studied by *X*-ray crystallography, also have the suggested structures.

## Experimental

The analytical procedures and physical measurements were carried out as previously described.[21]

*Preparation of the Complexes.*—Unless otherwise indicated, all complexes were prepared as follows. A warm ethanolic solution of the acetylpyridine (*ca.* 2*x* mol) was added, with magnetic stirring, to a warm solution of dehydrated $MX_2$ (*ca. x* mol) in anhydrous ethanol. The mixture was kept at *ca.* 60 °C, with continuous stirring, for a few minutes. After slowly cooling to room temperature, the solid compound was filtered off, washed with anhydrous ethanol and dried in a desiccator, under vacuum, over $P_4O_{10}$.

In the case of iodo-complexes, the solvent was preconditioned by addition of anhydrous $Na_2SO_3$, to prevent air oxidation of the iodide ion to any significant extent.

By this general method all the polymeric halogeno-complexes precipitated in a powdery form almost immediately after mixing the reagents. The colour of the filtrate was always different from that of the solid.

To prepare $[CoI_2(4\text{-}acpy)_2]$ the solution had to be concentrated under an i.r. lamp before the green solid crystallized out.

*Tetrakis*(3-*acetylpyridine*)*di-iodocobalt*(II), $[CoI_2(3\text{-}acpy)_4]$. This complex was prepared by the general method using 4*x* mol of 3-acetylpyridine for every *x* mol of cobalt(II) iodide. The mixture had to be kept in a refrigerator (*ca.* −18 °C) for several days to promote the formation of brownish red crystals.

*Isothiocyanato-complexes.* To a warm, filtered, saturated solution of $M(SCN)_2$ (*ca. x* mol) in ethanol an ethanolic solution of 3- or 4-acetylpyridine (2*x* mol) was added. After concentration of the mixture under an i.r. lamp to *ca.* one third of its volume and cooling to room temperature, either an oil or a solid was obtained. By rubbing the oil and cooling the mixture in a refrigerator (*ca.* −18 °C) a solid was formed. The solids were isolated from the mixture by filtration, washed with anhydrous ethanol, and dried in a vacuum desiccator over $P_4O_{10}$. The compounds so prepared, **(5)**, **(9)**, and **(14)**, were anhydrous. The highly coloured filtrates and washing liquids were mixed and kept in a refrigerator at *ca.* −18 °C. After *ca.* 2 d a solid had formed and the supernatant liquid was practically colourless. The solids were filtered off, washed with anhydrous ethanol, and air-dried. The solids, **(6)**, **(10)**, and **(15)**, were shown to contain two molecules of water, which persisted even after keeping the compounds for several days, under vacuum, in the presence of $P_4O_{10}$.

## Acknowledgements

We thank Dr. R. Perry (University of Manchester Institute of Science and Technology) for the C, H, and N analyses. We are deeply grateful to the late Professor S. M. Nelson for his invaluable help and advice in the discussion and interpretation of the results of this work. The financial support of the Instituto Nacional de Investigação Científica, Lisbon (Centro de Investigação em Química, Linha 3) is gratefully acknowledged.

## References

1 Y. Kidami, M. Noji, and H. Koike, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 239.
2 K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2301.
3 M. A. S. Goher, A. A. Hasanein, and G. M. Subruiti, *Bull. Soc. Chim. Fr.*, 1982, I-221.
4 M. G. B. Drew, N. I. Gray, M. F. Cabral, and J. de O. Cabral, *Acta Crystallogr., Sect. C*, 1985, **41**, 1434.
5 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd edn., John Wiley and Sons, New York, 1972.
6 S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 1965, 3276.
7 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.
8 A. R. Katritzky, A. R. Hands, and R. A. Jones, *J. Chem. Soc.*, 1958, 3165; A. R. Katritzky, C. R. Palmer, F. J. Swinborne, T. T. Tidwell, and R. D. Thompson, *J. Am. Chem. Soc.*, 1969, **91**, 636.
9 A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 1958, 2198.
10 Y. Kidami, M. Noji, and H. Koike, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 239.
11 A. E. Mahgoub, E. M. Khairy, and I. M. Kenawi, *Egypt. J. Chem.*, 1974, **17**, 829.
12 M. A. S. Goher, *Bull. Soc. Chim. Fr.*, 1981, I-329.
13 H-H. Wei and L-C. Men, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2301.
14 S. M. Nelson and T. M. Shepherd, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2123.
15 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley-Interscience, New York, 1963.
16 P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, 1968, **46**, 131.
17 M. A. S. Goher and A. Attia, *Acta Chim. Acad. Sci. Hung.*, 1980, **104**, 201.
18 A. Miezis, *Acta Chem. Scand.*, 1973, **27**, 3746.
19 W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and C. G. Christian, *J. Am. Chem. Soc.*, 1957, **79**, 5870.
20 G. J. Long, G. Galeazzi, U. Russo, G. Valle, and S. Calogero, *Inorg. Chem.*, 1983, **22**, 507.
21 M. F. Cabral and J. de O. Cabral, *J. Inorg. Nucl. Chem.*, 1977, **39**, 985.

*Received* 14*th January* 1987; *Paper* 7/071