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The Thermal Decomposition of Some Pyridine N-Oxide and Substituted Pyridine N-Oxide Complexes of Manganese(\parallel), Cobalt(\parallel), Nickel(\parallel), and Zinc(\parallel) Halides

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Pyridine *N*-oxide and substituted pyridine *N*-oxides form complexes with varied stoicheiometries with dipositive transition-metal halides. On controlled thermal decomposition, some manganese(II), cobalt(II), and nickel(II) complexes lose ligand to give stable phases with lower ligand content. Of these, monoligand complexes are most commonly isolated. Zinc(II) halide complexes give only a limited number of monoligand complexes on heating. The corresponding copper(II) halide monoligand complexes can be isolated directly from solution.

THE thermal decompositions of pyridine and substituted pyridine complexes with first-row transition-metal halides give a range of intermediate products containing progressively less ligand.¹ This work describes a similar investigation of the thermal decompositions of pyridine N-oxide and some substituted pyridine N-oxide complexes with transition-metal halides. The preparations of several of the initial complexes have been described ^{2,3} and their spectroscopic and magnetic properties reported. There has been little previous investigation of the thermal decompositions of pyridine N-oxide complexes.

EXPERIMENTAL

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The initial complexes were prepared by dissolving the hydrated metal halide in hot ethanol and adding a solution of the ligand in the same solvent, filtering the precipitate, and drying in vacuo. On occasion ether was added to facilitate precipitation. The course of the thermal decompositions was followed using a Stanton TR/1 Thermal Balance. All thermal decompositions were carried out in air. The reflectance spectra of the complexes in the range 13,500-28,500 cm.⁻¹ were measured on a Perkin-Elmer 450 Spectrophotometer with a diffuse reflectance accessory. The magnetic moments of the complexes were determined by the Gouy method with cobalt(II) tetrathiocyanatomercurate(II) as reference. Far-i.r. spectra were recorded on a R.I.I.C., F.S. 620 interferometer and Fourier Transform Computer (F.T.C. 100) working in the double-beam mode. The stable complexes formed during thermal decomposition were characterised by weight loss and analysis. Each compound prepared was analysed for metal, halide, carbon, and nitrogen. Halides and metals were estimated by standard techniques. Halide analyses only are included in Tables 1-4 (in parentheses beneath each compound).

RESULTS

The compounds prepared from solution and by thermal decomposition are listed in Tables 1—4. Those prepared but not included in the Tables are the zinc(II) salts which did not give monoligand thermal decomposition products. These were all of the type $Zn(ligand)_2X_2$ and most have been

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¹ J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1965, 27, 1865; *J. Chem. Soc.*, 1966, 1031, and refs. therein.

² J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, J. Amer. Chem. Soc., 1961, 83, 3770.

reported.³ Also not included are the copper salts which as prepared from solution were of the type Cu(ligand)X₂ but which did not give stable species with lower ligand content. They all had low magnetic moments (*ca.* 0.5 B.M.) with structures presumably similar to that of the binuclear pyridine *N*-oxide compound $[Cu(C_5H_5NO)Cl_2]_2$; many of these have been previously prepared.³ Some typical u.v. and visible spectra and magnetic moments of manganese(II), nickel(II), and cobalt(II) complexes are shown in Table 5.

The lists of compounds (Tables 1—3) are not restrictive. Complexes containing higher ratios of ligand to metal $[e.g., \text{Ni}(\text{pyO})_6\text{Cl}_2]$ have been prepared under different conditions.² However, as the main purpose of this investigation was the identification of complexes containing low ratios of ligand to metal, preparations giving high ligand content have not been included.

DISCUSSION

N-oxides can act as unidentate ligands as in $Zn(2,6-lutidine N-oxide)_2Cl_2$,⁴ or bridging ligands as in [Cu-(pyridine N-oxide)Cl_2]_2,⁵ and in Cu_3Cl_6(2-picoline N-oxide)_2,2H_2O.⁶ Pyridine is known to act as a unidentate ligand bonding through the nitrogen, and as pyridine N-oxide has the property of acting as a bidentate ligand, it should more readily form complexes with a low ratio of ligand to metal than does pyridine. In the presence of relatively weak complexing anions such as perchlorate or nitrate, cobalt(II), nickel(II), and zinc(II) form complexes with six N-oxide ligands for each metal,² as also do nickel(II) chloride, bromide, and iodides (anhydrous starting materials being used). If hydrated metal chlorides and bromides are used, hydrated complexes with less ligand are found.

The decomposition pattern ¹ for the pyridine complexes of the halides of manganese(II), cobalt(II), and nickel(II) is $M(L)_4X_2 \longrightarrow M(L)_2X_2 \longrightarrow M(L)X_2 \longrightarrow$ $M(L)_{\frac{3}{4}}X_2$. This pattern is not repeated with the *N*-oxide complexes. The majority of the complexes prepared from solution contain two ligand molecules for each metal atom, one of which is often solvent or water. However, in common with the pyridine series, a range of monoligand complexes can be prepared by thermal decomposition. There was some evidence from the

³ M. R. Kidd, R. S. Sager, and W. H. Watson, *Inorg. Chem.*, 1967, **6**, 946.

⁴ R. S. Sager and W. H. Watson, *Inorg. Chem.*, 1968, 7, 1358.
⁵ R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, 1967, 6, 951.

⁶ R. S. Sager and W. H. Watson, Inorg. Chem., 1968, 7, 2035.

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TABLE 1

| | 1909 | Manganese(11) complexes | | | | |
|--|------|---|---------------|---|------|---|
| Mn(pyO)Cl ₂ ,H ₂ O (29·6, 29·7) | | | 240° | Mn(pyO)Cl ₂ (31·9, 32·1) | 210 | $\begin{array}{c} \mathrm{Mn}(\mathrm{pyO})_{\frac{1}{2}}\mathrm{Cl}_{2}\\ (41\cdot3,\ 41\cdot0) \end{array}$ |
| | | $\frac{\operatorname{Mn}(\operatorname{pyO})_2\operatorname{Br}_2}{(39.1, 39.5)}$ $\operatorname{Mn}(\operatorname{pyO})_2\operatorname{I}_2$ | \rightarrow | | | $Mn(pyO)_{1}Br_{2}$ (61.4, 61.1) |
| | 160° | (50.2, 50.9) | | 16.00 | 240° | |
| $Mn(2-picO)Ol_2, H_2O$ (27.2 28.1) | 1300 | | | $Mn(2-picO)Cl_2$ (29.9 30.2) | 2409 | $Mn(2-picO)_{1}Cl_{2}$ (40.0 39.2) |
| $Mn(2-picO)Cl_2, H_2O$ (46.9, 46.8) | | | | $Mn(2-picO)Br_2$ (49.1, 49.4) | | $Mn(2-picO)_{1}Br_{2}$ (59.0, 59.3) |
| | | $Mn(2-picO)_2I_2$ | | (,, | | (,, |
| Mn/3 nicO)CL H O | 120° | (49.0, 48.1) | | Mn/2 picO)CI | | |
| (27.5, 28.1) | 120° | | | (30.4, 30.2) | | |
| $\frac{\mathrm{Mn}(3\text{-picO})\mathrm{Br}_2,\mathrm{H}_2\mathrm{O}}{(42\cdot8,\ 43\cdot2)}$ | | | | $\begin{array}{c} \text{Mn}(3\text{-picO})\text{Br}_2\\ (49\cdot1, 49\cdot4) \end{array}$ | | |
| | | $Mn(3-picO)_2I_2$ (48-9 49-1) | 9609 | | | |
| | | $Mn(4-picO)_2Cl_2$ | | Mn(4-picO)Cl ₂ | | |
| | | (20.1, 20.6) | 240° | (30.6, 30.2) | | |
| | | $Mn(4-picO)_2Br_2$ | | $Mn(4-picO)Br_2$ | | |
| | | (30.0, 37.0) | 240° | (49.1, 49.4) Mn(4 pic())I | | |
| | 1909 | $(48.4 \ 48.1)$ | | (60.4 60.8) | | |
| Mn(2.6-lutO)Cl., EtOH | | (10 1, 10 1) | | $Mn(2.6-lutO)Cl_{\bullet}$ | | |
| $(24 \cdot 4, 24 \cdot 1)$ | | | 200° | (28.0, 28.1) | | |
| | | $Mn(2, 6-lutO)_2Br_2$ | > | Mn(2,6-lutO)Br ₂ | | |
| | | (35.1, 34.9) | 210° | (47.5, 47.4) | | |
| | | $Mn (2,6-lutO)_2 I_2$ | > | $Mn(2,6-lutO)I_2$ | | |
| | | (45.7, 45.9) | | (58.3, 58.8) | | |

In this and other tables pyO = pyridine N-oxide, 2-picO = 2-picoline N-oxide, 3-picO = 3-picoline N-oxide, 4-picO = 4-picoline N-oxide, 2,6-lutO = 2,6-lutidine-N-oxide.

Figures in parentheses are the results of halide analyses. The first figure is that found, the second that calculated for the given stoicheiometry.

TABLE 2

| | Co | balt(11) complexes | s | |
|--|--------------|--|----------------------|--|
| Co(pyO)Cl ₂ , H ₂ O * (28•9, 29•2) Co(pyO)Br ₂ , H ₂ O (48•0, 48•2) | 170° 180° | | | Co(pyO)Cl ₂ (31·5, 31·6) Co(pyO)Br ₂ (51·1, 51·1) |
| Co(2-picO)Cl ₂ ,H ₂ O (27·3, 27·6) | 180° | (50.3, 50.5) Co(2-picO) ₂ Br ₂ | 220° | Co(2-picO)Cl ₂ (29·9, 29·7) Co(2-picO)Br ₂ |
| | 120° | $\begin{array}{c} (36\cdot4,\ 36\cdot6)\\ Co(2-picO)_{2}I_{2}\\ (48\cdot4,\ 47\cdot8)\\ Co(3-picO)_{2}Cl_{2}\\ (19\cdot9,\ 20\cdot4)\\ Co(3-picO)Br_{2}\\ (36\cdot3,\ 36\cdot6) \end{array}$ | 220° 260° 240° | $\begin{array}{c} (48.6, 48.4)\\ \mathrm{Co}(2\text{-picO})\mathrm{I}_2\\ (60.0, 60.2)\\ \mathrm{Co}(3\text{-picO})\mathrm{Cl}_2\\ (30.1, 29.7)\\ \mathrm{Co}(3\text{-picO})\mathrm{Br}_2\\ (48.5, 48.8)\end{array}$ |
| Co(3-picO) ₃ I ₂ (39·4, 39·6) | > | Co(3-picO) ₂ I ₂ (47·4, 47·8) | | Co(3-picO)I ₂ (59·8, 60·2) Co(4-picO)Cl ₂ (29·0, 29·7) Co(4-picO)Br ₂ (48·7, 48·8) Co(4-picO)I ₂ (50·7, 60·2) |
| | | Co(2,6-lutO)Cl ₂ ^b (27.0, 27.4) | | (03-1, 00-2) |
| | | | | Co(2,6-lutO)Br ₂ (46·3, 46·8) Co(2.6-lutO)I ₂ |
| | | | | (57.9, 58.3) |

^e Ref. 2. ^b H. M. Ramaswamy and H. B. Jonassen, Inorg. Chem., 1965, 4, 1595.



thermal decomposition data for monoligand complexes other than those in the Tables [e.g., (pyridine N-oxide)manganese(II) bromide] but where these compounds could not be obtained analytically pure they have not been listed. A limited number of complexes of empirical formula $M(L)_{\frac{1}{2}}Cl_2$, shown by X-ray powder photography to be distinct phases, were obtained.

The visible reflectance spectra and magnetic moments of the manganese(II) and nickel(II) complexes show that the metal ions are in a predominantly octahedral environment. Typical results are in Table 5.

For the cobalt(II) complexes, far-i.r. spectroscopy was in some cases more definitive in indicating metal

TABLE 4



environment than u.v. and visible spectroscopy. The complex CoCl₂(2,6-lutidine N-oxide), has a far-i.r. spectrum almost identical to that of the corresponding zinc compound whose structure is known to be tetrahedral;⁴ the metal-chloride stretching modes occur at 320 and 300 cm.⁻¹ in the former and 318 and 302 cm.⁻¹ in the latter. These values are close to those of the corresponding tetrahedral complex CoCl₂(pyridine)₂, namely 349 and 306 cm.^{-1,7} The bisligandcobalt(II) bromide

TABLE 5 Typical visible reflectance spectra (cm.⁻¹) and magnetic moments (B.M.)

Manganese(II)

| | | • | | | u - at | | | |
|---|-----------------|-------------------------|------------------------|-------------------------|------------------------|--|--|--|
| Complex | Colour | ${}^{4}T_{1a}(G)$ | ${}^{4}T_{2a}(G)$ | $^{4}A_{1a}(G)$ | 295°к | | | |
| Mn(pvO)Cl. H.O | Pink | 17.860 | 21.510 | 23.810 | 5.77 | | | |
| Mn(4-picO) _a Br _a | Pink | 17.860 | 21.370 | | 5.82 | | | |
| | | | , | | | | | |
| Nickel(II) | | | | | | | | |
| | | ${}^{3}T_{1a}(F)$ | ${}^{3}T_{1a}(P)$ | | | | | |
| Ni(pvO)Cl., H.O | Yellow | 13,700 | 22.200 | | 3.3 | | | |
| Ni(2.6-lutO),Br. | Blue | 14,600 | 23,800 | | 3.1 | | | |
| | | , | , | | | | | |
| Cobalt(II) (octahedral) | | | | | | | | |
| | | ${}^{4}A_{2a}(F)$ | ${}^{4}T_{1a}(P)$ | | | | | |
| Co(pvO)Cl.,H.O | Magenta | 17.540 | 20,880 | | 4.7 | | | |
| Co(4-picO)Cl, | Blue | 16,900 | 21,510 | | 4.8 | | | |
| , . | | | | | | | | |
| | Cobali | t(II) (tetra | hedral) | | | | | |
| | | 4T1 | (P) | | | | | |
| Co(2,6-lutO),Cl, | Blue | 15,100, | 16,950 | | 4.7 | | | |
| Co(2-picO) ₂ Br ₂ | Blue | 14,600, | 16,000 | | 4.6 | | | |
| The symbol | s in the l | neadings 1 | efer to t | he level | to which | | | |
| electron excita | ation occu | ırs. Ğrou | and state | s are: fo | or Mn ²⁺ - | | | |
| (octahedral), 6 | A_{1} ; for] | Ni ²⁺ (octah | edral), ³ A | l _{ea} ; for C | o ²⁺ (octa- | | | |

(octanedral), ${}^{*}A_{1g}$; for $N1^{2+}$ (octanedral), hedral), ${}^{4}T_{1g}$; for Co^{2+} (tetrahedral), ${}^{4}A_{2}$. tor 4_{2g};

complexes with 2-picoline N-oxide and 3-picoline N-oxide show strong peaks at 252 and 244 cm.⁻¹ and 250 and 240 cm.⁻¹ respectively. These are close to the values 278 and 258 cm.⁻¹ found for the tetrahedral com-

⁷ J. Bradbury, K. P. Forrest, R. H. Nuttall, and D. W. A. Sharp, Spectrochim. Acta, 1967, 23A, 2701.

plex $\operatorname{CoBr}_2(\operatorname{pyridine})_2$.⁷ None of the other cobalt(II) complexes examined showed strong peaks in those regions and these other complexes are therefore considered to contain halogen bridges and probably to have octahedral co-ordination about the metal. The u.v. and visible spectra of the mono-N-oxide monohydrate and monoligand complexes suggested predominantly octahedral environments for the cobalt(II).

A range of bisligandzinc(II) halide complexes has been examined by others ³ who have suggested that their structures might be tetrahedral or square planar. The structure of $ZnCl_2(2,6-lutidine N-oxide)_2$ has been confirmed as tetrahedral.⁴ The monoligand zinc(II) halide complexes do not show peaks in their far-i.r. spectra typical of tetrahedral terminal halide stretches and probably therefore have bridging halogens with more complex structures.

It is not possible to distinguish between complexes in which the pyridine N-oxide is acting as a terminal group and those in which it is bridging from the i.r. spectra associated with the ligand. Metal-oxygen modes have been observed⁸ in complexes of pyridine N-oxides between 350 and 450 cm.⁻¹ and we have found strong bands in this region. There is no systematic difference between the position and appearance of the band in View Article Online

copper complexes of low magnetic susceptibility where oxygen-bridging is expected and in zinc complexes of stoicheiometry ZnL_2X_2 where terminal pyridine *N*-oxide is found. The N-O stretching mode, which occurs near 1200 cm.⁻¹ in the spectra of all of these complexes, again cannot be used to provide an indication of structure.

On comparison of pyridine and pyridine N-oxide complexes, both ligands form an extensive array of monoand bis-ligand complexes. However, in spite of the ability of the N-oxides to act as bridging ligands, they form few complexes with less than one ligand present. This lack of complexes with low ratios of N-oxide to metal could be due to the high temperature, ca. 300°, required to prepare these derivatives, as at these temperatures the complexed N-oxide frequently decomposes. Although pyridine N-oxide can act as a bridging ligand with cobalt, nickel, and zinc, halogen bridges are formed when there is a low ratio of pyridine N-oxide to metal and it seems unlikely on steric grounds, although not established beyond doubt, that the pyridine N-oxide ligands are also bridging.

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⁸ R. Whyman and W. E. Hatfield, *Inorg. Chem.*, 1967, **6**, 1859; R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chem. Acta*, 1967, **1**, 113.