The Chemistry of 2-Pyridylamine Complexes of Cobalt(II) and Cobalt(III)

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Experimental details of the $^4T \rightleftharpoons {}^2E$ ' equilibrium ' for the complex $[Co^{II}(tpa)_2](ClO_4)_2$ (tpa = tri-2-pyridylamine) are given together with temperature-dependence studies of the magnetic behaviour of the hexafluorophosphate salt and of the corresponding 4-, 5-, and 6-methyl-substituted tri-2-pyridylamine complexes of cobalt(II) which prove to be magnetically normal. Factors influencing spin-crossover situations in cobalt(II) chemistry are briefly discussed. New cobalt(III) complexes of the above ligands are reported and some substitution and redox reactions of these complexes are briefly considered. Details of new cobalt(III) complexes of di-2-pyridylamine(dpa) are given, including a material of empirical composition $[Co(dpa)_2(O_2)](ClO_4)$.

GOODGAME[1] has investigated complexes of cobalt(II) with di-2-pyridylamine (dpa) but no report of cobalt(III) derivatives has been published. Tri-2-pyridylamine (tpa) may function as a vicinal terdentate ligand and complexes with the cobalt(II) ion are known.[2-4] Bis(tri-2-pyridylamine)cobalt(II) perchlorate is of particular interest since this has been shown to exist in two spin states.[5] The detailed magnetic behaviour[5] of the complex resembles that of di-isothiocyanatobis(1,10-phenanthroline)iron(II),[6] and of the polymorphs of the corresponding iron(II) 2,2′-bipyridine complex, more closely than that of other well documented examples of spin-crossover situations in cobalt(II) complexes.[7] Thus on warming from liquid-nitrogen temperatures, when the ^2E state is the lower in energy, a spin change occurs over a *narrow* range of temperature and on further warming to 373 K the effective magnetic moment increases beyond the value expected for true degeneracy of the ^4T and ^2E states. The fact that the magnetic properties of the bis(tri-2-pyridylamine)-cobalt(II) cation are dependent on the counter ion (the hexafluorophosphate salt obeys the Curie–Weiss law[5]) does however parallel observations with bis(2,2′,2″-terpyridyl)cobalt(II) complexes.[8]

We recently synthesised some methyl-substituted derivatives of tri-2-pyridylamine[9] and in this paper we investigate the effect of these modifications to the ligand on the magnetic behaviour of the cobalt(II) perchlorate complexes. We also examine the possibility of synthesising some cobalt(III) complexes of these terdentate ligands, as well as providing experimental details relevant to our earlier communication.[5]

EXPERIMENTAL

Chemicals were commercial specimens except for the tri-2-pyridylamines which were prepared as previously reported.[9] Complexes of tri-2-pyridylamine were prepared by literature methods[2] and the nickel(II) and iron(II) complexes used for comparison of i.r. spectra were those characterised earlier.[10]

Preparations.—Cobalt(II) *complexes of tri-2-pyridylamine* (tpa). Bis(tri-2-pyridylamine)cobalt(II) perchlorate was prepared as previously reported.[2] The complex was recrystallised from nitromethane–benzene. To prepare the hexafluorophosphate salt the following procedure was adopted. Basic cobalt carbonate was added in small portions to a solution of hexafluorophosphoric acid (0·4 cm^3; *ca.* 1 mmol diluted with an equal volume of water) until effervescence ceased. The mixture was filtered and to the filtrate was added a solution of tpa (0·50 g; 2 mmol) in ethanol (7 cm^3). The precipitated *complex* was purified by repeated dissolution in nitromethane followed by reprecipitation with benzene.

Cobalt(II) *complexes of* 4-, 5-, *and* 6-*methyl*-2-*pyridyldi*-2-*pyridylamine* (4-Mepdpa, 5-Mepdpa, 6-Mepdpa). Cobalt(II) perchlorate hexahydrate (0·35 g) in triethyl orthoformate (10 cm^3) was added to the appropriate ligand (0·7 g) in triethyl orthoformate (10 cm^3) and gently warmed for 2—3 min. A buff-coloured *solid* was deposited which was filtered off and washed with ethanol.

Cobalt(III) *complexes of* 4- *and* 5-*methyl*-2-*pyridyldi*-2-*pyridylamine.* Cobalt(II) perchlorate hexahydrate (0·35 g) in ethanol (10 cm^3) was added to the appropriate ligand (0·7 g) in ethanol (10 cm^3). A few drops of hydrogen peroxide solution (30%) were added to the reaction mixture together with sodium perchlorate (0·2 g), after which the solution was heated under reflux for 15 min. On setting the solution aside a yellow *product* deposited. The crude material was recrystallised from acetone–ethanol to afford bright yellow crystals. Attempts to prepare cobalt(III) complexes of tpa by this and other methods failed presumably due to the immediate precipitation of the cobalt(II) complex which failed to react further. However the lowish magnetic moment of the hexafluorophosphate salt as prepared above may arise from slight cobalt(III) contamination.

Cobalt(III) *complexes of di-2-pyridylamine: di-μ-peroxo-tetrakis*(*di-2-pyridylamine*)*dicobalt*(III) *perchlorate.* Tris(di-2-pyridylamine)cobalt(II) perchlorate (0·5 g), prepared following Goodgame,[1] in ethanol (10 cm^3) was heated under reflux with hydrogen peroxide (1 cm^3, 30%) for 10 min.

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[1] M. Goodgame, *J. Chem. Soc.* (*A*), 1966, 63.

[2] W. R. McWhinnie, G. C. Kulasingam, and J. C. Draper, *J. Chem. Soc.* (*A*), 1966, 1199.

[3] G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc.* (*A*), 1967, 1253.

[4] G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc.* (*A*), 1968, 254.

[5] P. F. B. Barnard, A. T. Chamberlain, G. C. Kulasingam, W. R. McWhinnie, and R. J. Dosser, *Chem. Comm.*, 1970, 520.

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[8] J. S. Judge and W. A. Baker, jun., *Inorg. Chim. Acta*, 1967, **1**, 245.

[9] J. C. Lancaster and W. R. McWhinnie, *J. Chem. Soc.* (*C*), 1970, 2435.

[10] J. C. Lancaster and W. R. McWhinnie, *J. Chem. Soc.* (*A*), 1970, 2673.

The solution first became dark brown, then greenish, and on setting aside a red-brown *product* deposited. This was recrystallised from ethanol.

Attempted synthesis of dihalogenobis(di-2-pyridylamine)-cobalt(III) *complexes.* The above peroxo-complex (0·3 g) was treated with concentrated hydrochloric acid (2 cm^3). The colour changed from red-brown to greenish brown after which water (10 cm^3) was added and the mixture was then heated under reflux for 5 min. On setting the solution aside a pale green complex deposited. The product was washed with water but no recrystallisation solvent was found. The complex dissolved in hot water to afford a brownish solution from which no well defined material could be isolated. Analysis suggested the stoicheiometry $[Co(dpa)_2Cl_2](ClO_4)$,dpa, 2HCl,H_2O. Use of hydrobromic acid in the above preparation gave a brownish complex of composition $[Co(dpa)_2Br_2]Br,H_2O$.

Reaction with ammonium thiocyanate. Bis(5-methyl-2-pyridyldi-2-pyridylamine)cobalt(III) perchlorate (0·5 g) in ethanol (10 cm^3) was added to a saturated ethanolic solution of ammonium thiocyanate (10 cm^3). The mixture was set aside for 10 min at room temperature when the solution became orange and deposited an orange-brown solid. The complex was filtered off and washed with ethanol but all attempts at recrystallisation resulted in decomposition. The complex analysed approximately for $[\{(5\text{-}Mepdpa)Co\}_2(NCS)_3](ClO_4)_3,H_2O$. When the above reaction mixture was heated under reflux for 10 min the solution turned yellow, then green, finally depositing a bright green solid which was filtered off and washed with ethanol. Analysis indicated the formulation $[\{(5\text{-}Mepdpa)Co\}_2(NCS)_3][Co(NCS)_4](ClO_4),H_2O$. In both the above cases i.r. support for the presence of water was noted.

TABLE 1

Analytical data (%) for 2-pyridylamine complexes of cobalt(II) and cobalt(III)

Complex	Found			Calc.			Λ_M [a]	μ_{eff} [b]
	C	H	N	C	H	N		
$[Co^{II}(tpa)_2](ClO_4)_2$	47·7	3·2	15·1	47·8	3·2	14·8		4·74
$[Co^{II}(tpa)_2](PF_6)_2$	42·2	2·5	13·2	42·4	2·8	13·2		4·36
(1) $[Co^{II}(4\text{-}Mepdpa)_2](ClO_4)_2,H_2O$	48·5	3·8	14·3	48·0	3·7	14·0	135 [c]	4·25—4·45
(2) $[Co^{II}(5\text{-}Mepdpa)_2](ClO_4)_2,H_2O$	47·5	3·4	14·2	48·0	3·7	14·0	150 [c]	4·12—4·54
(3) $[Co^{II}(6\text{-}Mepdpa)_2](ClO_4)_2$	48 7	3·6	14·4	49·1	3·6	14·3	157 [c]	4·85
(4) $[Co^{III}(4\text{-}Mepdpa)_2](ClO_4)_3$	44·0	3·4	13·3	43·6	3·2	12·8	225 [c]	0·15
(5) $[Co^{III}(5\text{-}Mepdpa)_2](ClO_4)_3,H_2O$	42·4	3·4	12·9	42·7	3·3	12·5	220 [c]	0·0
(6) $[Co^{III}(4\text{-}Mepdpa)(NO_2)_3],2H_2O$	38·6	3·3	20·2	38·8	3·6	19·8	25 [c]	0·0
(7) $[Co^{III}(5\text{-}Mepdpa)(NO_2)_3],4H_2O$	35·5	3·9	18·4	36·1	4·1	18·3	15 [c]	0·2
(8) $[Co^{III}(4\text{-}Mepdpa)_2][Co^{II}(OH)_4]ClO_4,7H_2O$ [d]	39·8	3·6	11·4	40·7	5·1	11·9	214 [c]	4·3
(9) $[\{Co^{III}(5\text{-}Mepdpa)\}_2(NCS)_3](ClO_4)_3,H_2O$	38·7	3·0	13·1	37·4	2·6	13·7	230 [c]	0·8
(10) $[\{Co^{III}(5\text{-}Mepdpa)\}_2(NCS)_3][Co^{II}(NCS)_4]ClO_4,H_2O$	38·8	2·4	16·8	38·3	2·4	17·2	180 [c]	4·5
(11) $[(dpa)_2Co(O_2)_2Co(dpa)_2](ClO_4)_2$	45·0	3·8	15·8	45·1	3·5	15·8	150 [e]	0·2
(12) $[Co(dpa)_2Cl_2]ClO_4,dpa,2HCl,H_2O$	43·2	3·7	15·5	43·3	3·5	15·2	70 [c]	0·0
(13) $[Co(dpa)_2Br_2]Br,H_2O$	35·7	3·0	12·4	36·4	3·0	12·7	170 [c]	0·0

dpa = Di-2-pyridylamine, tpa = tri-2-pyridylamine, and 4-, 5-, and 6-Mepdpa = 4-, 5-, and 6-methyl-2-pyridyldi-2-pyridylamine.

[a] Molar conductivity/Ω^{-1} cm^2 mol^{-1}. [b] Room-temperature moment/B.M. Where water is said to be present, appropriate i.r. absorptions are seen. [c] Nitromethane solution. [d] Found: Co, 12·5. Calc. Co, 12·55%. [e] Dimethylformamide solution.

Attempts to Isolate Oxidation Intermediates.—Several attempts were made, by varying reaction conditions, to isolate possible intermediates in the oxidation of cobalt(II) to cobalt(III) in the above syntheses. One experiment reproducibly afforded a complex containing cobalt in both oxidation states. Cobalt(II) perchlorate hexahydrate (0·35 g) in acetone (10 cm^3) was added to 4-Mepdpa (0·7 g) in acetone (10 cm^3). The solution was heated under reflux for 15 min and then set aside overnight. A green product was deposited which was recrystallised from ethanol and for which available data suggest the formula $[Co(4\text{-}Mepdpa)_2][Co(OH)_4]ClO_4,7H_2O$.

Reactions of the Cobalt(III) *Complexes.*—(*4-Methyl-2-pyridyldi-2-pyridylamine*)*trinitrocobalt*(III). Bis(4-methyl-2-pyridyldi-2-pyridylamine)cobalt(III) perchlorate (0·5 g) in ethanol (10 cm^3) was heated under reflux for 10 min with a saturated ethanolic solution of sodium nitrite (10 cm^3). The yellow solid dissolved and the colour of the solution became orange. On setting aside for 30 min an orange *product* deposited. The complex was recrystallised from ethanol and analysed as the dihydrate. A similar procedure using $[Co(5\text{-}Mepdpa)_2](ClO_4)_2$ afforded $[Co(5\text{-}Mepdpa)](NO_2)_3,4H_2O$.

Analytical data are given in Table 1 and other physical data pertinent to complexes of cobalt(II) are in Table 2 and to complexes of cobalt(III) in Table 3.

Physical Measurements.—I.r. spectra (4 000—250 cm^{-1} were measured on Nujol mulls or potassium bromide discs using a Perkin-Elmer 457 spectrophotometer. Low-frequency i.r. data (400—200 cm^{-1}) were obtained with a Perkin-Elmer 225 instrument. Spectra at −185 °C were measured using the R.I.I.C. variable-temperature i.r. unit (VLT 2). Electronic spectra were recorded for powdered specimens with a Unicam SP 700 spectrophotometer fitted with the SP 735 reflectance attachment. Conductivity measurements were made using 10^{-3}M solutions of the complexes in pure nitromethane or dimethylformamide with a Henelec bridge. Magnetic measurements were by the Gouy method. For some complexes the variation of molar susceptibility with temperature was followed using the Newport apparatus in the Chemistry Department, University of Reading. This equipment was used by kind permission of Dr. D. Rice. Measurements on the two tpa complexes were made with similar equipment at University College, Bangor, in collaboration with Dr. R. J. Dosser. No dependence of susceptibility

TABLE 2

Electronic spectra (for new complexes) and magnetic data for cobalt(II) complexes of tri-2-pyridylamine and methyl-substituted tri-2-pyridylamines

Complex (see Table 1)	Electronic spectrum (kK)			Magnetic properties as a function of temperature [$10^6\chi_M$ (c.g.s.u.), μ_{eff} (B.M.), T (K)]
	$^4T_{1g} \longrightarrow {}^4T_{2g}$	$^4T_{1g} \longrightarrow {}^2T_{1g}(G)$	$^4T_{1g} \longrightarrow {}^4T_{1g}(P)$	
$[Co(tpa)_2](ClO_4)_2$				7 771, 4·82, 373·4; 8 735, 4·83, 333·2; 9 573, 4·74, 293·3; 10 807, 4·63, 253·2; 11 808, 4·48, 213·2; 11 864, 4·28, 193·0; 10 345, 3·78, 173·3; 10 359, 3·79, 173·2;* 8 652, 3·37, 163·9; 7 202, 2·97, 153·3; 5 887, 2·50, 133·2; 5 684, 2·27, 113·1; 6 212, 2·15, 93·1
$[Co(tpa)_2](PF_6)_2$				6 383, 4·36, 373·1; 7 190, 4·38, 333·2; 7 972, 4·36, 297·9; 9 586, 4·40, 253·2; 11 213, 4·37, 213·2; 12 398, 4·38, 193·2; 13 845, 4·38, 173·1; 15 563, 4·36, 153·1; 17 581, 4·33, 133·3; 20 538, 4·31, 113·2, 24 185, 4·30, 93·1
(1)	11·6	19·0sh	22·5	
(2)	11·7	18·8sh	22·1sh	7 169, 4·12, 293; 7 498, 4·06, 273; 8 271, 4·03, 244; 9 270, 4·01, 215; 11 244, 3·99, 177; 12 344, 3·95, 157; 14 094, 3·96, 138; 15 424, 3·83, 118; 17 744, 3·79, 99
(3)	10·8	18·9	22·9	9 935, 4·85, 293; 10 844, 4·80, 263; 11 834, 4·73, 235; 13 074, 4·67, 206; 14 064, 4·60, 187; 15 134, 4·51, 167; 16 624, 4·45, 148; 18,484, 4·38, 128; 24 954, 4·23, 89

* Measurement repeated after allowing sample to warm up.

on field strength was observed, nor did the susceptibility of the perchlorate complex show any time dependence.

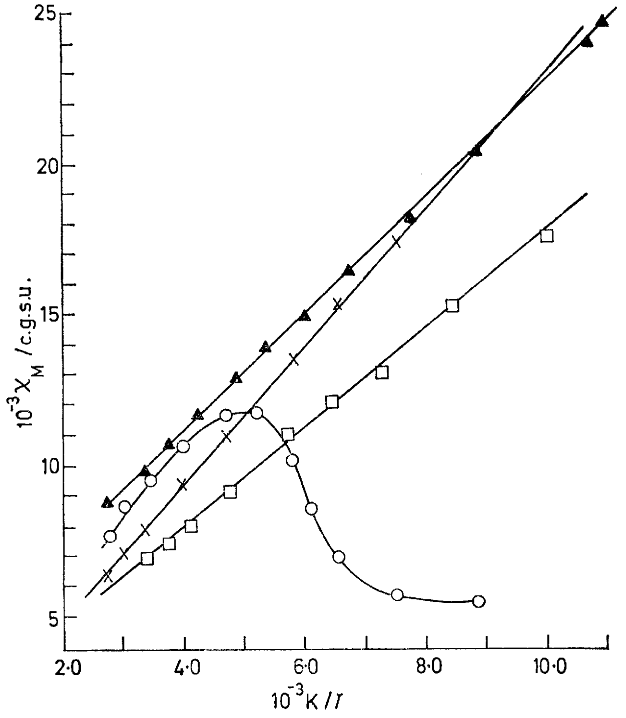
TABLE 3

Electronic spectra of some 2-pyridylamine complexes of cobalt(III)

Complex (see Table 1)	Electronic spectrum (kK)
(4)	22·0
(5)	16·4w,sh, 22·1
(6)	14·9w,sh, 22·0sh
(7)	14·3w,sh, 22·0sh
(8)	7·6, 15·7, 16·8; 22·1
(9)	8·5w,sh, 23·0
(10)	7·5, 16·0, 23·0
(11)	15·3sh, 19·2
(12)	17·5, 26sh
(13)	9·6w, 16·2sh, 25·0v.br, sh

RESULTS AND DISCUSSION

Cobalt(II) *Complexes*.—It was hoped that the slightly greater values of the ligand-field splitting parameter, Δ, for 4- and 5-methyl-2-pyridyldi-2-pyridylamine (4-Mepdpa and 5-Mepdpa), compared to that of tri-2-pyridylamine (tpa),[10] together with the low-symmetry component of the ligand field arising from the presence of the methyl groups, might combine to favour the ^2E state of the cobalt(II) ion. Initial preparations of the complex $[Co(5\text{-}Mepdpa)_2](ClO_4)_2$ showed room-temperature moments as low as 4·12 B.M. (Table 1), hence we determined the temperature dependence of the susceptibility (Table 2) for this complex. Plots of χ_M against $1/T$ were linear (Figure) and no change in spin state was observed over the temperature range 293—99 K. It was then found that other specimens of the complex, although analytically and spectroscopically (i.r. and electronic) identical to that above, gave higher values of the effective magnetic moment. Barnard[5,11] has demonstrated that quite drastic changes occur in the low-frequency i.r. spectrum when the complex $[Co(tpa)_2](ClO_4)_2$ undergoes change of spin state on cooling. In particular the spectrum, initially similar



Plot of χ_M against T^{-1}: (○), $[Co(tpa)_2](ClO_4)_2$; (×), $[Co(tpa)_2](PF_6)_2$; (□) $[Co(5\text{-}Mepdpa)_2](ClO_4)_2$; and (▲), $[Co(6\text{-}Mepdpa)_2](ClO_4)_2$

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[11] P. F. B. Barnard, Ph.D. Thesis, University of Aston in Birmingham, 1972.

to that of [Ni(tpa)$_2$](ClO$_4$)$_2$, becomes similar to that of [Fe(tpa)$_2$](ClO$_4$)$_2$ ($^1A_{1g}$ ground state) on cooling. Thus we examined the i.r. spectra (600—200 cm^{-1}) of the two series [M(5-Mepdpa)$_2$](ClO$_4$)$_2$ and [M(4-Mepdpa)$_2$](ClO$_4$)$_2$ (M = Fe^{II},[10] Co^{II}, or Ni^{II} [10]) at both 293 and 88 K. In both series the major difference between the spectra at the two temperatures was the superior resolution obtained on cooling. However, although the data indicate that no change in spin state occurs for the complex [Co(5-Mepdpa)$_2$](ClO$_4$)$_2$ or for [Co(4-Mepdpa)$_2$](ClO$_4$)$_2$, we observed that the two cobalt complexes did show some weak bands corresponding in position to major bands in the spectra of the iron complexes which were absent from the spectra of the nickel complexes. Thus it appeared that some low-spin species was present in a small enough quantity to just affect μ_{eff} without interfering with the goodness of fit of the analytical data. It is now known (see below) that cobalt(III) complexes [Co^{III} (4- or 5-Mepdpa)$_2$](ClO$_4$)$_3$, are readily prepared and that their far i.r. spectra are very similar indeed to those of the iron(II) complexes of the ligands. Thus it is certain that the low-spin contaminant in some preparations of [Co(4- or 5-Mepdpa)$_2$](ClO$_4$)$_2$ is the corresponding cobalt(III) complex. The fact that higher values of μ_{eff} are obtained when the cobalt(II) complexes are prepared in the absence of air is in accord with this.

Not only does change of the anion from ClO$_4^-$ to PF$_6^-$ remove the anomalous magnetic behaviour of the complex [Co(tpa)$_2$](ClO$_4$)$_2$, but also the introduction of substituents does likewise despite the fact that simple argument led us to anticipate that the ^2E state would be more favoured in these cases. We wondered if an even more subtle modification would remove the anomalous magnetic behaviour of [Co(tpa)$_2$](ClO$_4$). Accordingly we grew dilute crystals of the complex in the diamagnetic and isomorphous zinc(II) complex. The magnetic properties of the resulting crystals paralleled precisely those of [Co(tpa)$_2$](ClO$_4$)$_2$.

We suggested earlier that the difference between the magnetic behaviours of the salts [Co(tpa)$_2$]X$_2$ (X = ClO$_4^-$ or PF$_6^-$) may reflect the differing abilities of the two lattices to accommodate the expected distortion from cubic symmetry [12] of the low-spin form, which would remove the degeneracy of the ^2E state. On these grounds the substituted ligands should be more, not less, effective in stabilising the low-spin form since there is already present a low-spin component in the ligand field.[10] The failure of the ion [Co(bipy)$_3$]$^{2+}$ (bipy = 2,2'-bipyridine) to show anomalous magnetic behaviour could then be attributed to the rigid D_3 symmetry of the complex; however the recent structural determination for [Cu(bipy)$_3$](ClO$_4$)$_2$ [13] shows these tris(chelate) complexes to be less rigid than suspected and implies that the [Co(bipy)$_3$](ClO$_4$)$_2$ lattice at least should be able to accommodate a distortion from D_3 symmetry to remove the ground-state degeneracy in a low-spin form. It becomes clear that no simple explanation of the observations reported here can be advanced at this juncture.

6-Methyl-2-pyridyldi-2-pyridylamine (6-Mepdpa) is a weaker ligand in the spectrochemical sense than the 4- and 5-methyl isomeric compounds.[10] Thus we were not surprised to find that there was no evidence of a spin crossover for the complex [Co(6-Mepdpa)$_2$](ClO$_4$)$_2$ on cooling (Table 2), the Curie–Weiss law being obeyed over the temperature range considered. Electronic spectra of the cobalt(II) complexes are listed in Table 2. The lowest-frequency band may be assigned as $^4T_{1g} \longrightarrow {}^4T_{2g}$ (ν_1) and the band between 22 and 23 kK as $^4T_{1g} \longrightarrow {}^4T_{1g}$ (P) (ν_3). Use of Lever's [14] graphical method then gives values of Δ of 12·95 kK (4- and 5-Mepdpa) and 12·1 kK (6-Mepdpa) and of the reduced Racah parameter B' of *ca.* 800 cm^{-1} (4- and 5-Mepdpa) and *ca.* 900 cm^{-1} (6-Mepdpa). Apart from the fact that the complex [Co(6-Mepdpa)$_2$](ClO$_4$)$_2$ seems less covalent than [Ni(6-Mepdpa)$_2$](ClO$_4$)$_2$, these data agree well with values estimated with respect to nickel(II).[10] The above values of Δ and B' lead us to expect the weak two-electron transition $^4T_{1g} \longrightarrow {}^4A_{2g}$ (ν_2) close to 23 kK; hence the shoulder observed close to 19 kK is probably a spin-forbidden transition $^4T_{1g}(^4F) \longrightarrow {}^2T_{1g}(^2G)$ similar to that observed for tris(di-2-pyridylamine)cobalt(II) perchlorate.[1]

Cobalt(III) *Complexes*.—In contrast to our experience with tpa we found that complexes of 4- and 5-Mepdpa with cobalt(III) were readily prepared. They are bright yellow diamagnetic materials which dissociate as 1 : 3 electrolytes in nitromethane when prepared as the perchlorate salts (Table 1). The electronic spectrum shows one spin-allowed *d–d* band at *ca.* 22 kK (Table 3) for both the complexes [Co(4-Mepdpa)$_2$](ClO$_4$)$_3$ and [Co(5-Mepdpa)$_2$](ClO$_4$)$_3$ which may be assigned in the terminology of O_h symmetry as $^1A_{1g} \longrightarrow {}^1T_{1g}$. Under our experimental conditions no splitting of the band was observed. Higher-frequency *d–d* bands are masked by ligand absorptions. The position of the $^1A_{1g} \longrightarrow {}^1T_{1g}$ band may be compared with that for [Co(bipy)$_3$]$^{3+}$ at 22·3 kK.[15]

We briefly investigated the reactivity of the new cobalt(III) complexes of substituted tri-2-pyridylamines with nucleophiles such as the nitrite ion. Substitution reactions proceeded smoothly with the precipitation of uncharged complexes [(6) and (7), Table 1]. Analytical data support the given formulations and i.r. spectroscopy [16] indicates the presence of nitro- rather than nitrito-groups; also the electronic spectrum (Table 3) is consistent with a CoN$_6$ chromophore.

The reaction between the complex [Co^{III}(5-Mepdpa)$_2$](ClO$_4$)$_3$ and ammonium thiocyanate in the cold afforded a material which analysed somewhat imperfectly for

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$[\{Co^{III}(5\text{-Mepdpa})\}_2(NCS)_3](ClO_4)_3,H_2O$ [(9), Table 1]. The magnetic moment of 0·8 B.M. may arise from a temperature-independent contribution but is more probably associated with contamination by cobalt(II) since the complex is readily converted to complex (10) (Table 1). The green complex, (10), clearly contains the tetraisothiocyanatocobaltate(II) anion both from magnetic (Table 1) and spectroscopic (Table 3) evidence {*cf.* $Hg[Co(NCS)_4]$ and $(Me_4N)_2[Co(NCS)_4]$: 7·8 and 16·3 kK}.[17] In this instance, rather more compelling analytical support is obtained for the formulation $[\{Co^{III}(5\text{-Mepdpa})\}_2(NCS)_3][Co^{II}(NCS)_4],(ClO_4),H_2O$. The fact that both complexes (9) and (10) show a band at 23·0 kK lends support to the view that they contain a common cation.

Since we failed to isolate any complex that might reasonably be regarded as an intermediate in the oxidation of cobalt(II) to cobalt(III) using substituted tri-2-pyridylamines, we decided to investigate the oxidation of tris(di-2-pyridylamine)cobalt(II) perchlorate.[1] In this instance we were able to isolate a brown material [(11), Table 1] which was diamagnetic and which had the stoicheiometry $Co(dpa)_2(O_2)ClO_4$. The presence of a peroxo-group is indicated by a strong i.r. band at 885 cm^{-1} which is not characteristic of the organic ligand and which may be assigned as $\nu(O-O)$.[18] The choice between a monomeric (Λ_M 75 Ω^{-1} cm^2 mol^{-1}, dmf) or a dimeric structure (Λ_M 150 Ω^{-1} cm^2 mol^{-1}, dmf) is not easily made on the basis of conductivity measurements since the above figures are, or could be, consistent with either 1 : 1 or 1 : 2 electrolytes. We have used the dimeric formulation in Table 2 since the precidents in cobalt(III) chemistry are for bridging rather than chelating peroxo-groups, however di-μ-peroxo-complexes are rare, even ethylenediamine for example affords a μ-ethylenediamine-μ-peroxo-intermediate.[19] This complex should be an interesting subject for an *X*-ray crystallographic study.

The reaction of peroxo-complexes of cobalt(III) and ethylenediamine[19] or other polyamines[20] with strong hydrochloric acid usually affords the thermodynamically less-stable *trans*-isomer of the dichloro-complex. In the case of dpa a recent crystal structure of bis(di-2-pyridylamine)copper(II) perchlorate[21] showed the copper(II) ion to be in a distorted tetrahedral environment and this has cast doubt on the feasibility of a *trans*-configuration for these ligands. However rather more general surveys of the chemistry of the copper(II) ion with bidentate pyridylamine ligands[2,22,23] suggest that the flexibility of the chelate ring may be sufficient to allow a *trans*-stereochemistry in some cases. We thought that treatment of the peroxo-complex considered above with concentrated hydrochloric and hydrobromic acids would be worth considering. The reaction reproducibly afforded the two complexes (12) and (13) listed in Table 1. The presence of protonated di-2-pyridylamine in (12) is suggested by the i.r. spectrum, in particular an N–H band at 3 390 cm^{-1} is characteristic of this species. Complex (12) contains perchlorate ions, but apparently in complex (13) the bromide ion is sufficiently large to effect precipitation. The diamagnetism excludes the possible presence of a cobalt(II) species. We examined the far i.r. spectra of the two complexes but these were so complex that confident assignment of cobalt–halogen vibrations was not possible. If the complexes are *trans*-dihalogeno-compounds, it should be possible to isomerise them to the *cis*-isomers. Repeated dissolution in water and evaporation to dryness led to the recovery of the unchanged complexes.

We thank the S.R.C. (J. C. L.) and the University of Aston in Birmingham (M. E. F. and P. F. B. B.) for research studentships.

[3/018 *Received, 2nd January*, 1973]

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