Substituted Phenols as Ligands. Part V[1]. Six Co-ordinate Cobalt(II) and Nickel(II) Adducts with Nitrogen Bases and Water

J. I. BULLOCK and R. J. HOBSON,

Joseph Kenyon Laboratories, Department of Chemistry, The University of Surrey, Guildford, Surrey, U. K.
Received December 23, 1975

The preparation and properties of nickel(II) and cobalt(II) complexes of phenolates with 2-methoxy, 2-ethoxy, and 2,6-dichloro- substituents as adducts with pyridine, N,N,N¹,N¹-tetramethylethylenediamine, and water are reported. The electronic spectra and magnetic moments for the nickel(II) complexes are consistent with octahedral, weak field stereochemistry but those for the high spin cobalt(II) compounds are less readily explained. Isomorphism is found for one pair of complexes suggesting that the stereochemical arrangements of both metal ions are similar. Large distortions from regular octahedral (O_h) symmetry would account for the properties observed for the cobalt(II) compounds.

Introduction

Little is known of the co-ordination chemistry of the phenolic oxygen atom to divalent metal ions except when it forms part of a larger chelating system as in salicylaldehyde or Schiff bases.

2-Methoxyphenolates, in which the ethereal oxygen atom might be regarded as a potentially weak donor, are known from crystallographic analysis to co-ordinate through both the phenolic and methoxy oxygen atoms in the complexes bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) hydrate[2], bis(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II)[1], and bis(2-methoxy-4-nitrophenolato)N,N,N¹,N¹-tetramethylethylenediaminecopper(II) dihydrate[3]. Large distortions from regular, octahedral (O_h) stereochemistry are found in each case. For instance, the methoxy oxygen atoms co-ordinate at an angle of *ca.* 70° to the plane containing the phenolic oxygen and nitrogen atoms and at a greater distance than the in-plane atoms.

The 2,6-dichloro substituents do not co-ordinate in bis(2,4,6-trichlorophenolate) N,N,N¹,N¹-tetramethylethylenediaminecopper(II)[1] and the complex is essentially square-planar.

There are a few reports of nickel(II)[4-6] and cobalt(II)[7] complexes with ligands containing methoxy groups in the co-ordination sphere. Bis(methoxyacetato)diaquonickel(II)[5] is six-co-ordinate with short

Ni–O(CH₃) bonds (Ni–O(CH₃), 1.99Å; Ni–O(H₂), 2.07Å; Ni–O(CO), 2.05Å) whereas the five-co-ordinate dibromo-[1-(2-methoxyphenyl)-2,6-diazaoctane] nickel(II)[6] has a much longer Ni–O(CH₃) bond (2.318 Å). It would seem[5] that the longer distances reported for methoxy groups contained in carboxylate anions co-ordinated to copper(II) are not caused by either steric hindrance or by the inherent weakness of the methoxy oxygen donor atom. From studies[1-3] to date it is not clear whether the same is true for methoxy groups bonded to an aromatic nucleus.

The present work is an extension of previous[1-4, 8] studies on the range and stereochemistries of complexes formed by substituted phenols.

Results and Discussion

Analytical results are given in Table I. The diffuse reflectance spectra were recorded over the range 30000–4500 cm⁻¹ (Figures 1 and 2). Those included in the Figures span the range of observations. Further details[9] of the spectra have been deposited in the University of Surrey Library*. Better resolution was obtained on recording the spectra at low temperature.

Nickel(II) Complexes (Figure 1)

The electronic, *d–d*, absorption spectrum of nickel (II) in weak octahedral (O_h) fields usually consists of three spin-allowed transitions: v_1, $^3T_{2g} \leftarrow {}^3A_{2g}$ (7000–13 000 cm⁻¹); v_2, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (11 000–20 000 cm⁻¹); and v_3, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (19 000–27 000 cm⁻¹). The position of v_1 gives a reasonable estimate of the crystal field parameter 10Dq.

A large number of tetragonal six-co-ordinate complexes are known for which the above transitions should appear as doublets. In practice the transitions to the two higher states of O_h symmetry often appear as rather broad single bands but resolution of the components is sometimes obtained at low temperature[10]. The v_1 transition frequently splits into two

---

* Enquiries should be addressed to the Librarian, The University of Surrey, Guildford, Surrey. The usual loan charges will be made.

TABLE I. Physical and Spectral Data.

Spectroscopic Results for the Cobalt and Nickel Complexes[a]

No.	Compound	Colour	$Dq(cm^{-1})$[b]	v_2/v_1[b]
(i)	$Co(N)_2(py)_2$	Brown	990	2.15
(ii)	$Co(V)_2(py)_2$	Green	960	2.16
(iii)	$Co(T)_2(py)_2$	Mauve	860	1.99
(iv)	$Co(P)_2(py)_2$	Purple	875	1.96
(v)	$Co(T)_2Meen$	Purple	905	2.04
(vi)	$Co(V)_2(H_2O)_2$	Brown	880	2.06[c]
(vii)	$Co(B)_2(H_2O)_2$	Mauve	875	2.09[c]
(viii)	$Co(N)_2(H_2O)_4$	Yellow	1105	–
(ix)	$Ni(N)_2(py)_2$	Green	840	
(x)	$Ni(V)_2(py)_2$	Green	870	
(xi)	$Ni(N)_2Meen$	Green	820	
(xii)	$Ni(T)_2(py)_2$	Yellow	700	
(xiii)	$Ni(P)_2(py)_2$	Yellow	710	
(xiv)	$Ni(T)_2(py)_2(H_2O)_4$	Blue	960	
(xv)	$Ni(P)_2(py)_2(H_2O)_4$	Blue	940	
(xvi)	$Ni(T)_2Meen(H_2O)_4$	Blue	920	

Analytical Results

No.	Calculated (%)					Found (%)				
	M	C	H	N	H_2O	M	C	H	N	H_2O
(i)	10.65	52.1	4.0	10.1	–	10.5	51.9	3.9	10.4	–
(ii)	11.35	60.1	4.65	5.4	–	11.3	60.2	4.6	5.3	–
(iii)	9.65	43.3	2.3	4.6	–	9.8	43.1	2.2	4.5	–
(iv)	7.9	35.35	1.35	3.75	–	7.8	35.5	1.3	3.7	–
(v)	10.4	38.05	3.55	4.95	–	10.5	37.8	3.5	4.9	–
(vi)	14.85	48.4	4.55	–	9.05	14.7	48.3	4.6	–	8.6
(vii)	13.85	50.85	5.2	–	8.45	14.1	50.8	5.2	–	9.2
(viii)	12.6	36.0	4.3	6.0	15.4	12.8	35.9	4.2	6.0	14.4
(ix)	10.6	52.1	4.0	10.1	–	10.7	52.0	4.0	10.1	–
(x)	11.3	60.15	4.65	5.4	–	11.2	59.9	4.6	5.4	–
(xi)	11.5	47.0	5.5	10.95	–	11.5	46.8	5.7	10.8	–
(xii)[d]	9.6	43.35	2.3	4.6	–	9.6	43.2	2.7	4.6	–
(xiii)[e]	7.85	35.35	1.35	3.75	–	7.8	35.5	1.4	3.6	–
(xiv)	8.6	38.75	3.25	4.1	10.55	8.7	–	–	–	–
(xv)	7.15	32.25	2.2	3.4	8.8	7.2	–	–	–	–
(xvi)	9.2	33.8	4.4	4.4	11.25	–	33.6	4.4	4.4	11.0

[a] N = 2-methoxy-4-nitrophenolato; V = 4-formyl-2-methoxyphenolato; B = 2-ethoxy-4-formylphenolato; T = 2,4,6-tri-chlorophenolato; P = pentachlorophenolato; Meen = N,N,N^1,N^1-tetramethylethylenediamine; py = pyridine. [b] At room temperature. [c] The band assigned to v_2 is less intense than a band found near 16 600 cm^{-1}. [d] Cl. calc. 34.9; found 34.9%. [e] Cl. calc. 47.4; found 47.3%.

components which may be assigned, for example, in D_{4h} symmetry to transitions from the ground state to the $^3B_{2g}$ and ^3E_g states. In many other cases[11], the spectra of nickel(II) complexes with several different donor atoms retain the simple form found in O_h symmetry.

Two weak spin-forbidden bands may be observed, one of which is usually close to v_2[12] and can be well defined especially if Dq/B is near to unity as is the case for the $Ni(H_2O)_6^{2+}$ ion.

In the present work, the complexes gave spectra (Figure 1) with three band maxima in the region 7000–20 000 cm^{-1} assignable to the v_1, v_2, and v_3 transitions in O_h symmetry although the true symmetry in all cases must be much lower than this.

The anhydrous chlorophenolate complexes, (xii) and (xiii) alone had two bands of near equal intensity assignable to the components of v_2 but since there was no splitting of v_1 one of these was probably a spin-forbidden transition.

The Dq values (Table I) which increased as the temperature was lowered, classified the complexes into three groups:

(1) the anhydrous chlorophenolate complexes with pyridine, (xii) and (xiii) in Table I.

(2) the methoxyphenolate complexes with pyridine and N,N,N^1,N^1-tetramethylethylenediamine, (ix), (x), and (xi).
and

(3) three hydrated chlorophenolate complexes with pyridine and N,N,N^1,N^1-tetramethylethylenediamine as additional ligands. These appeared (Figure 1) to exhibit a large splitting of ν_1 to give a band near 9500 cm^{-1} and a weak one near 4500 cm^{-1}. For ions with A_2 ground states graphs[13] are available which depict the variation predicted in the various transition frequency ratios with Dq/B and E(ν_3)/B. Using these it is possible to calculate the expected position of any one transition from the observed positions of the other two. In a typical example, the following were obtained at room temperature for bis(2,4,6-trichlorophenolato)-di(aquo)bis(pyridine)nickel(II) dihydrate, compound no. (xiv), assuming $\nu_1 = 9600$ cm^{-1}.

Observed; ν_1, 9600 cm^{-1}; ν_2, 15 900 cm^{-1}; ν_3, 26 100 cm^{-1}.

(a) From ν_1 and ν_2

$B = 1000$ cm^{-1}, ν_3(calc) $= 28\ 100$ cm^{-1}

(b) From ν_1 and ν_3

$B = 881$ cm^{-1}, ν_2(calc.) $= 15\ 500$ cm^{-1}

(c) From ν_2 and ν_3

$B = 832$ cm^{-1}, ν_1(calc.) $= 9900$ cm^{-1}

and (d)

From $B = (\nu_2 + \nu_3 - 3\nu_1)/15$ and Dq $= 960$ cm^{-1}.

$B = 887$ cm^{-1}, ν_2(calc.) $= 15\ 650$ cm^{-1},
ν_3(calc.) $= 26\ 300$ cm^{-1}.

With the exception of (a), the calculated and observed results compared favourably and the agreement was as good at that obtained[13] for the Ni(H$_2$O)$_6^{2+}$ ion. Therefore, the lower frequency band near 4500 cm^{-1} was not assignable to a component of ν_1.

Including the methoxyphenolate complexes reported earlier[4] the order of Dq values for a total of sixteen complexes was:

$$Ni(X)_2(L)_2 \cdot 4H_2O > Ni(Y)_2 \cdot 2H_2O \cong Ni(Y)_2(L)_2 > Ni(Y)_2 > Ni(X)_2(L)_2$$

| Dq 960–920 | 920–780 | 870–820 | 740–730 | 710–700 cm^{-1} |

(where X = a chlorophenolate , Y = a methoxyphenolate, and L = pyridine or $^1/_2$ Meen).

The magnetic moments of the nickel(II) complexes (Table II) confirmed the weak field, six-co-ordinate nature of the stereochemistry.
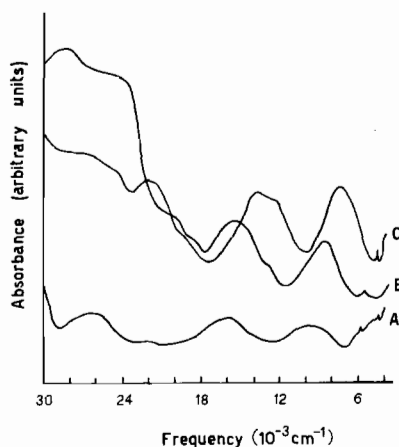

Figure 1. Diffuse reflectance spectra of the Nickel(II) complexes, Curve A, Ni(T)$_2$(py)$_2$(H$_2$O)$_4$; B, Ni(N)$_2$(py)$_2$; C, Ni(T)$_2$(py)$_2$ (recorded at low temperature).
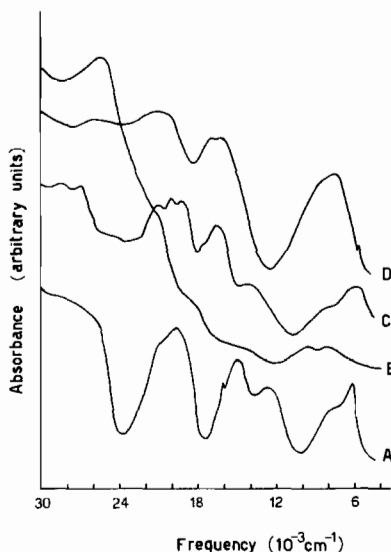
Figure 2. Diffuse reflectance spectra of the Cobalt(II) complexes. Curve A, Co(T)$_2$(py)$_2$; B, Co(N)$_2$(H$_2$O)$_4$; C, Co(B)$_2$(H$_2$O)$_2$; D, Co(V)$_2$(py)$_2$ (recorded at low temperature).

On the basis of these results and the crystallographic[1-3] work with copper(II), possible structural schemes are proposed assuming that the 2,6-chloro substituents do not co-ordinate: (a) The hydrated chlorophenolates would have four short Ni–O bonds from two phenolato

TABLE II. Variation with Absolute Temperature of Atomic Susceptibilities (c.g.s.u.) and Magnetic Moments (B.M.).

$Co(N)_2(py)_2$	$\Theta = 10°$					
T(K)	288	230.5	166.5	135	103.5	89
$10^6\chi_A$	9057	11270	15240	18560	23890	27380
μ_{eff}	4.57	4.56	4.50	4.48	4.45	4.42
$Co(V)_2(py)_2$	$\Theta = 0°$					
T(K)	292.5	230	198.5	166	136	89.5
$10^6\chi_A$	9150	11490	13320	15900	19550	29460
μ_{eff}	4.62	4.60	4.60	4.59	4.61	4.59
$Co(T)_2(py)_2$	$\Theta = 7°$					
T(K)	292.5	230.5	166	136	103.5	90
$10^6\chi_A$	10010	12170	16200	19540	25050	28710
μ_{eff}	4.84	4.73	4.64	4.61	4.55	4.54
$Co(P)_2(py)_2$	$\Theta = 7°$					
T(K)	292.5	230.5	184.5	145.5	105.5	90
$10^6\chi_A$	8917	11080	13780	17380	23490	27510
μ_{eff}	4.57	4.52	4.51	4.50	4.45	4.45
$Co(T)_2Meen$	$\Theta = 3°$					
T(K)	292.5	229	193	165	90	
$10^6\chi_A$	8910	11190	13190	15370	27630	
μ_{eff}	4.56	4.53	4.51	4.50	4.46	
$Co(N)_2(H_2O)_4$	$\Theta = 7°$					
T(K)	292.5	230.5	184	135.5	104	89
$10^6\chi_A$	9266	11550	14290	19180	24600	28030
μ_{eff}	4.65	4.61	4.58	4.56	4.52	4.47
$Co(V)_2(H_2O)_2$	$\Theta = 9°$					
T(K)	292	230.5	185.5	145.5	103.5	89.5
$10^6\chi_A$	9153	11340	14010	17240	24220	27670
μ_{eff}	4.62	4.57	4.56	4.48	4.47	4.45
$Co(B)_2(H_2O)_2$	$\Theta = 8°$					
T(K)	292	230	184.5	145.5	105.5	90
$10^6\chi_A$	10150	12760	15950	20120	26820	31090
μ_{eff}	4.87	4.84	4.85	4.84	4.76	4.73
$Ni(N)_2(py)_2$	$\Theta = 0°$					
T(K)	292.5	230.5	166.5	135	103.5	89.5
$10^6\chi_A$	4331	5427	7603	9355	12200	14200
μ_{eff}	3.18	3.16	3.18	3.17	3.18	3.19
$Ni(V)_2(py)_2$	$\Theta = 0°$					
T(K)	291.5		166.5	136	104	89.5
$10^6\chi_A$	4284		7509	9104	12220	13850
μ_{eff}	3.16		3.16	3.14	3.18	3.15
$Ni(T)_2(py)_2$	$\Theta = 0°$					
T(K)	292	234.5	184	145.5	103.5	89.5
$10^6\chi_A$	4298	5320	6903	8608	12100	14220
μ_{eff}	3.17	3.16	3.18	3.16	3.16	3.18

$Ni(P)_2(py)_2$	T(K),	292.5;	$10^6\chi_A$,	4406;	μ_{eff},	3.21
$Ni(N)_2Meen$	T(K),	292;	$10^6\chi_A$,	4454;	μ_{eff},	3.22
$Ni(P)_2(py)_2 \cdot 4H_2O$	T(K),	292;	$10^6\chi_A$,	4340;	μ_{eff},	3.18
$Ni(T)_2Meen \cdot 4H_2O$	T(K),	292;	$10^6\chi_A$,	4646;	μ_{eff},	3.28
$Ni(T)_2(py)_2 \cdot 4H_2O$	T(K),	292.5;	$10^6\chi_A$,	4296;	μ_{eff},	3.17

and two water ligands with two Ni–N bonds, (b) the hydrated methoxyphenolates, six short Ni–O bonds derived from two bidentate phenolates with two Ni–OH$_2$ bonds, and (c) the methoxyphenolates with nitrogen bases, two short Ni–O bonds to the phenolate oxygen atoms and two Ni–O bonds from the methoxy oxygen atoms, possibly lengthened slightly because of the presence of two nitrogen donor atoms. The remain-

ing anhydrous complexes would be polymeric, the methoxyphenolates, $Ni(Y)_2$, with four bonds derived from bidentate chelating methoxyphenolate ions and two long bonds from bridging phenolate oxygens, and the chlorophenolates, $Ni(X)_2(L)_2$, with nitrogen bases four bonds to oxygen from bridging phenolate ligands and two Ni–N bonds.

Cobalt(II) Complexes (Figure 2)

Three spin-allowed *d–d* transitions are expected[14] for octahedral (O_h) high-spin cobalt(II) complexes which arise from transitions to $^4T_{2g}(\nu_1)$, $^4A_{2g}(\nu_2)$, and $^4T_{1g}(P)(\nu_3)$ states from the $^4T_{1g}$ ground state. In many cases ν_1 is observed as a weak band relative to ν_3, in the near i.r. region and ν_3 (near 20 000 cm^{-1}) usually has associated shoulders. Either the $^4A_{2g} \leftarrow$ $^4T_{1g}$ transition is not observed or it is very weak and assignments should be made with caution. The theoretical value[14] of the frequency ratio, ν_2/ν_1, is almost invariant at 2.1–2.2 which aids assignment.

The presence of low symmetry components in the ligand field usually gives rise to more complex spectra with band splitting and higher intensities[15]. Spin-forbidden transitions and spin–orbit coupling variation can also complicate the spectra.

Six-co-ordinate, high-spin complexes usually have room temperature effective magnetic moments in the range 4.7–5.2 B.M. which are greater than the spin-only value (3.87 B.M.) and decrease slightly as the temperature is lowered. A detailed discussion is given by Figgis[16]. Our spectra (Figure 2) and magnetic measurements (Table II) did not fit these patterns. The diffuse reflectance spectra had more bands than are usually observed for high-spin, octahedral (O_h) cobalt (II). The near i.r. absorption (ν_1) had two components or was asymmetric, several bands of relatively high intensity were found in the ν_2 region, and multiple absorptions were seen for ν_3 as is often the case.

Bis(2-methoxy-4-nitrophenolato) tetraaquocobalt (II) had a different spectrum from the other cobalt complexes. The ν_1 absorption was split but very weak (Figure 2) and ν_2 was not observed although a ligand absorption may have interferred.

The effective magnetic moments at room temperature (Table II) were in the range 4.56–4.87 B.M. and fell slightly with temperature to give small values of the Curie–Weiss constant, Θ. These were at or below the low end of the range usually observed for high-spin, six-co-ordinate cobalt(II).

X-ray powder photographs of all the cobalt(II)–pyridine complexes and their nickel(II) analogues were examined for evidence of isomorphism. This was found between one pair of compounds, Co(N)$_2$(py)$_2$ and Ni(N)$_2$(py)$_2$. All of the cobalt(II) complexes, with one exception (*vide supra*) have very similar spectra. Thus isomorphism in one case establishes the co-ordination number of cobalt(II) in all the complexes as six, since the spectral and magnetic properties of Ni (N)$_2$(py)$_2$ are consistent only with six co-ordination.

Taking the arithmetic mean of the split near i.r. absorptions in the cobalt(II) spectra and allowing[17] that $\nu_1 \cong 8$ Dq (as in O_h symmetry), the calculated Dq values (Table I) were higher than those for the nickel (II) complexes with equivalent ligand sets as would be expected[18]. The order of the Dq values was not the same as for nickel(II) but a smaller number of complexes was considered. Thus the order of Dq values was:

$$Co(Y)_2(L)_2 > Co(Y)_2(H_2O)_2 \cong Co(X)_2(L)_2$$

Dq 990, 960   880, 875   905, 875, 860 cm^{-1}
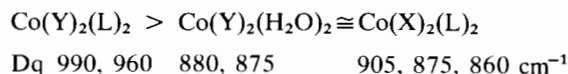
(where X, Y, and L have the same significance as for the nickel complexes).

Multiple absorptions for ν_2 are not expected[17]. With the exception cited above all the spectra show a band in the ν_2 region which gives an acceptable ν_2/ν_1 ratio (1.96–2.16) based upon the arithmetic mean of the ν_1 absorptions (Table I). Such a calculation assists the assignment of six-co-ordination and is approximately valid[19] if the distortion from O_h symmetry is not too large. The band attributable to ν_2 is often found to be more intense than expected[20] in six-co-ordinate cobalt (II) complexes having symmetry lower than O_h. The remaining bands in the ν_2 region may be spin-forbidden transitions or may be a result of deviations from O_h symmetry. They are a common feature[20–22] of the spectra of low symmetry six-co-ordinate cobalt(II) complexes.

The magnetic results are readily explained in terms of a low symmetry component to the ligand field. Low symmetry six-co-ordinate cobalt(II) complexes are known[15,20,22] which have magnetic moments in the range normally associated with tetrahedral compounds. The lowering in moment is due to the splitting of the $^4T_{1g}$ ground state of O_h symmetry which results in a reduction of orbital contribution[15,16] to the moment. If the X-ray crystallographic structures were known it would be possible to give a more accurate description of the magnetic results when allowance could be made for the distortions.

Experimental

The abbreviations are explained in Table I. Where possible A.R. grade materials were used. The melting points of the phenols were checked before use and most were recrystallised.

Cobalt(II) Complexes

These were either adducts with nitrogen bases or hydrates.

Method 1 – Nitrogen base complexes.

The nitrogen base (0.02 mol equivalent) was added to a filtered solution of the appropriate phenol (0.021 mol) in aqueous sodium hydroxide solution (0.02 mol, 100 ml). To this was added with stirring a solution of cobalt(II) sulphate heptahydrate (0.01 mol) in water (100 ml). The resultant precipitate was filtered off by suction, washed with water (4 × 20 ml) and dried in vacuo (CaCl$_2$). Yields in excess of 85% were obtained.

Method 2 – Hydrated complexes.

A solution of anhydrous cobalt(II) chloride (0.005 mol) in propan-2-ol (100 ml) was added dropwise with stirring to a filtered solution of the appropriate phenol (0.0105 mol) in aqueous sodium hydroxide solution (0.01 mol, 100 ml). The resultant precipitate was filtered by suction, washed with ethanol (96%, 4 × 5 ml) and dried at the pump. Drying was completed over P_4O_{10}.

Necessary modifications of method 1 are given below.

Bis(4-formyl-2-methoxyphenolato)bis(pyridine) cobalt(II)

A dark green tarry substance was obtained when the general method was applied. Treatment of this with ethanol or the incorporation of ethanol in the reaction mixture gave $Co(V)_2(H_2O)_2$. A portion of $Co(V)_2$ $(H_2O)_2$ (1.80 g) was dissolved in pyridine (18 ml). Light petroleum (70 ml, 100–120°C) was added followed by diethyl ether (300 ml) to give a green solution. This was filtered and reduced to about half volume when a green solid began to separate. On cooling, a dark green microcrystalline solid was deposited. This was filtered off, washed with light petroleum (5 ml, 40–60°C) and dried at the pump. Drying was completed over P_4O_{10} and fresh wax shavings. The yield was 50%.

Bis(2-methoxy-4-nitrophenolato)bis(pyridine) cobalt(II)

The general method gave a mixture of $Co(N)_2(py)_2$ and $Co(N)_2(H_2O)_4$. Pyridine (0.04 mol) was added to a filtered solution of potassium 2-methoxy-4-nitrophenolate monohydrate (0.01 mol) in water (70 ml) and ethanol (96%, 30 ml). To this was rapidly added with stirring, a solution of cobalt(II) nitrate hexahydrate (0.005 mol) in ethanol (90%, 50 ml). A brown microcrystalline solid separated slowly. After five minutes stirring this was filtered off and dried at the pump for 30 minutes. Drying was completed over P_4O_{10}.

Nickel(II) Complexes

Most of the nickel complexes were prepared by a general method analogous to that used for the cobalt (II) complexes except that nickel(II) nitrate hexahydrate was used. Drying conditions varied widely. Following the numbering method shown in Table I:

Compound No.	Drying method
(ix)	*Vacuo*, $CaCl_2$
(x)	see text
(xi)	*Vacuo*, $CaCl_2$
(xii)	*Vacuo*, P_4O_{10}, see text
(xiii)	*Vacuo*, P_4O_{10}, see text
(xiv)	see text
(xv)	air dried
(xvi)	$CaCl_2$

Bis(2,4,6-trichlorophenolato)diaquobis (pyridine)nickel(II) Dihydrate (xiv)

This was prepared as a light blue solid which partially decomposed on drying. The dried material was recrystallised from ethanol (96%) and water (3:2) containing pyridine (2% by volume). The crystals were filtered off, washed with a little ethanol/water (3:2) and press dried between filter papers. Finally air drying was employed.

Bis(2,4,6-trichlorophenolato)bis(pyridine) nickel(II) (xii)

Dehydration of the tetrahydrate gave the air stable solid.

Bis(pentachlorophenolato)bis(pyridine) nickel(II) (xiii)

Dehydration of the tetrahydrate gave the solid.

Bis(4-formyl-2-methoxyphenolato)bis(pyridine) nickel(II)   *(x)*

The general method gave a tarry substance which could not be recrystallised. Pyridine (0.025 mol) was added to a filtered solution of 4-formyl-2-methoxyphenol (0.011 mol) in aqueous sodium hydroxide solution (0.01 mol, 70 ml) and methanol (50 ml). To this was added with stirring a solution of nickel(II) nitrate hexahydrate (0.005 mol) in water (50 ml). An apple green solid separated overnight. This was filtered off, washed with methanol/water (1:1, 2 × 5 ml) and dried at the pump. It was finally dried over P_4O_{10}.

Analyses

Analytical methods were standard (Table I).

Physical Methods

(a) Spectra were obtained routinely using a Unicam SP700C spectrophotometer. (b) Magnetic susceptibilities were determined using a Newport Instruments Variable Temperature Guoy Balance. (c) Thermogravimetric analysis was performed in an atmosphere of dry nitrogen using a modified Stanton HT-D thermobalance. (d) Powder photographs were obtained routinely using Cu K_α radiation ($\lambda = 1.542$ Å).

References

1 Part IV, J.I. Bullock, R.J. Hobson and D.C. Povey, *J.C.S. Dalton*, 2037 (1974).

2 R.J. Hobson, M.F.C. Ladd and D.C. Povey, *J. Cryst. Molecular Struct., 3*, 377 (1973).

3 M.F.C. Ladd and D.C. Povey, to be published.

4 J.I. Bullock and S.L. Jones, *J. Chem. Soc. A*, 2472 (1970).

5 C.K. Prout, C. Walker and F.J.C. Rossotti, *J. Chem. Soc. A*, 556 (1971).

6 P.L. Orioli and M. Di Vaira, *J. Chem. Soc. A*, 2078 (1968).

7 F.A. Cotton and R.H. Holm, *J. Am. Chem. Soc., 82*, 2979 (1960).

8 J.I. Bullock and S.L. Jones, *J. Chem. Soc. A,* 2351 (1971).

9 R.J. Hobson, *Ph. D. Thesis,* University of Surrey, 1973.

10 See, for example, D.A. Rowley and R.S. Drago, *Inorg, Chem., 6,* 1092 (1967).

11 A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p. 337.

12 Ref. 11, p. 333.

13 Ref. 11, p. 216 and 392.

14 Ref. 11, p. 318.

15 A.B.P. Lever, *Inorg. Chem., 4,* 1042 (1965).

16 B.N. Figgis, "Introduction to Ligand Fields", Interscience, New York, 1966, p. 248.

17 Ref. 11, p. 112.

18 Ref. 16. p. 244.

19 A.B.P. Lever and D. Ogden, *J. Chem. Soc. A*, 2041 (1967).

20 R. Whyman, W.E. Hatfield and J.S. Paschal, *Inorg. Chim. Acta, 1,* 113 (1967).

21 D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem., 4,* 721 (1965).

22 F.A. Cotton, D.M.L. Goodgame and R.H. Soderburg, *Inorg. Chem., 2,* 1162 (1963).