Inorganica Chimica Acta, 25 (1977) 191–202

Complexes of Binucleating Ligands. IX. Some Tetranuclear Nickel(II), Cobalt(II) and Mixed Cobalt(II)–Cobalt(III) Complexes

R. ROBSON and D. G. VINCE*

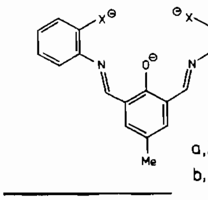
The Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

Received January 8, 1977

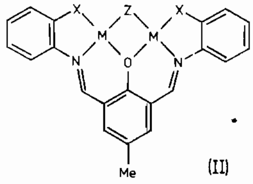
A number of nickel(II), cobalt(II) and mixed cobalt(II)–cobalt(III) derivatives of the trianionic binucleating ligand (L^{3-}) derived from 2-hydroxy-5-methylisophthalaldehyde di-2′-hydroxyanil (LH_3) have structures based on a tetranuclear $[LM_2(X)]_2$ core where X^- = OH^- or OR^-. Additional ligands may occupy four "axial" coordination sites, one on each metal centre, provided by the $[LM_2(X)]_2$ core. In some cases loss of these axial ligands generates square pyramidal centres which for nickel(II), may be either high-spin or low-spin. Variable numbers of protons (up to three) may be attached to the basic tetranuclear core, e.g. *three protons in $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$ and one proton in $[LNi_2(OH)]_2(NO_3)(H)$. Compounds with the following formulations were isolated and studied in 2-methoxyethanol solution by osmometric, conductimetric, titrimetric and spectroscopic techniques and in the solid phase by spectroscopic and magnetic techniques: $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$, $[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$, $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$, $[LNi_2(OH)]_2(NO_3)(H)$, $[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$ (C_5H_5N = pyridine), $[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$ ($C_3H_4N_2$ = pyrazole), $[LNi_2(OH)\cdot LNi_2(OR)]_2$ (R = CH_3 or $CH_2CH_2OCH_3$), $[LCo^{II}_2(OH)]_2(CH_3CO_2)_2(H)_2$, $[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2$, $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2$.*

Introduction

Some cupric complexes of the trianionic binucleating ligand, Ia (hereafter L^{3-}), derived from 2-hydroxy-5-methylisophthalaldehyde di-2′-hydroxyanil (LH_3) have been previously described [1]. The complexes were of the general composition LCu_2Z and of the general structure II [M = Cu, X = O and Z^- = OH^-, OR^-, $C_3H_3N_2^-$ (pyrazolate anion)]. Subsequently, the incorporation of a much wider range of bridging species, Z, into complexes of the type II (X = S, M = Cu^{II}, Ni^{II}) was reported [2].



(I)
a,X=O
b,X=S



(II)

Attempts to trap dioxygen at the bridging site of a binuclear cobalt(II) derivative of Ia by the process, $(Co^{II})_2 + O_2 \rightarrow (Co^{III})_2(O_2^{2-})$, yielded mixed cobalt(II)–cobalt(III) products and no evidence for the retention of the oxygen–oxygen bond was obtained. The X-ray crystal structure determination of one of the products (namely, $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 2H_2O\cdot 2C_2H_5OH$) was the subject of a preliminary publication [3] and revealed the tetranuclear structure for the discrete molecule $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2$ represented in Fig. 1.

In the present report we describe the cobalt complexes of L^{3-} more fully and also some closely related nickel(II) complexes which appear to contain a similar tetranuclear core. The behaviour of these nickel complexes contrasts sharply with that of the cupric complexes of the same ligand [1] and also with that of both cupric and nickel(II) complexes of the related ligand Ib [2].

Results and Discussion

Initial attempts to prepare nickel(II) and cobalt(II) analogues of the previously reported methoxy-bridged cupric complex, $LCu_2(CH_3O)$ [1] under analogous conditions, *i.e.* by reaction between LH_3 and the divalent acetate in hot methanol (air being excluded in the cobalt(II) case), gave products of formulation $[LM_2(OH)]_2(CH_3CO_2)_2(H)_2$ where H represents an acidic hydrogen atom. Attempts to generate nickel complexes incorporating the bridging

---

*Present address: ICI Australia Ltd., Central Research Laboratories, Ascot Vale, Victoria 3032, Australia.

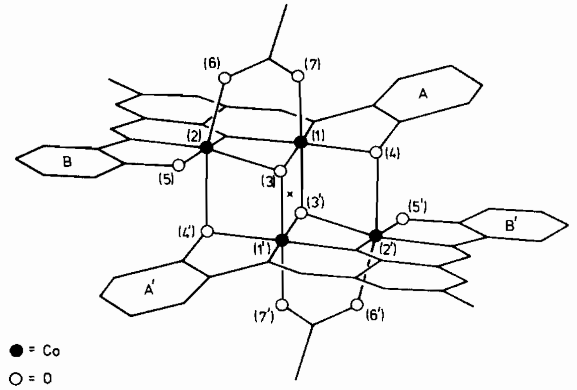


Figure 1. A representation of the structure of the centrosymmetric molecule $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2$ [3]. ● = Co, ○ = O, * = centre of symmetry. Co(1) and Co(1') are Co(III). Co(2) and Co(2') are Co(II). O(3) and O(3') are OH^-. Bond lengths in Å: Co(1)–O(3'), 1.89; Co(1)–O(7), 1.90; Co(2)–O(4'), 2.24; Co(2)–O(6), 2.01. L units are twisted from planarity so that the normal to ring A (and A') makes an angle of approx. 21° to the mean plane through the donor atom set, whilst ring B (and B') is almost coplanar with the donor set.

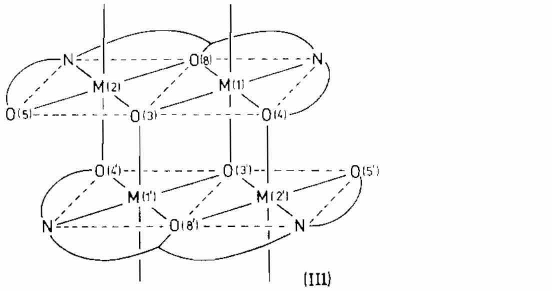
species $C_3H_3N_2^-$ (pyrazolate anion), Cl^- and NO_2^- yielded respectively $[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$, $[LNi_2(OH)]_2(CH_3CO_2)Cl_2(H)_3$ and $[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$ in which, we now believe, these species do not play their intended bridging role. The isolation of a pyridine adduct, $[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$, of composition analogous to that of the pyrazole complex, supports the view that the latter contains neutral $C_3H_4N_2$ as a monodentate donor, rather than $C_3H_3N_2^-$ as a bridging species. The compound $[LNi_2(OH)]_2(NO_3)(H)$ with only a single acidic hydrogen atom was generated inadvertently by reaction of LH_3 with the mixed nitrate–n-butyrate salt, $Ni(C_4H_7O_2)(NO_3)(C_4H_8O_2)3H_2O$, in attempts to prepare butyrate derivatives which, it was hoped, might be more soluble in organic solvents than the corresponding acetates. Two complexes lacking acidic hydrogen atoms formulated (see below) as $[LNi_2(OH)\cdot LNi_2(OCH_3)]_2$ and $[LNi_2(OH)\cdot LNi_2(OCH_2\cdot CH_2\cdot O\cdot CH_3)]_2$ could be obtained from methanolic and 2-methoxyethanolic solutions respectively, by the action of hydroxide ion on any of the nickel complexes above, except the pyrazole adduct. All of the above complexes were highly hygroscopic and, as described below, differences in properties of anhydrous and hydrated materials were, in some cases, significant.

Reaction of $[LCo_2^{II}(OH)]_2(CH_3CO_2)_2(H)_2$ with dioxygen in methanolic solution yielded the methoxy-bridged complex $[LCo^{II}Co^{III}(CH_3O)]_2(CH_3CO_2)_2\cdot 2H_2O$ whereas reaction in aqueous ethanol yielded the hydroxy-bridged species $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 2H_2O$. The dioxygen uptake accompanying these reactions was much less than expected on the basis of the anticipated incorporation as peroxide of one dioxygen per binuclear unit, and amounted to 91 ± 6% of that predicted for the following process in which only half the cobalt centres are oxidised to cobalt(III) and dioxygen is reduced to the water level:

$$[LCo_2^{II}(OH)]_2(CH_3CO_2)_2(H)_2 + 2CH_3OH + \tfrac{1}{2}O_2$$
$$\rightarrow 3H_2O + [LCo^{II}Co^{III}(CH_3O)]_2(CH_3CO_2)_2$$

Attempts to grow crystals of $[LCo^{II}Co^{III}(CH_3O)]_2(CH_3CO_2)_2$ suitable for X-ray crystallography from aqueous ethanol gave a mixture of the hydroxy-bridged complex $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 2C_2H_5OH\cdot 2H_2O$ with the molecular structure [3] shown in Fig. 1 together with an unidentified diamagnetic product. The cobalt in the latter was presumably entirely in the III oxidation state but the oxidised cobalt products isolated and identified had properties consistent with the cobalt(II)–cobalt(III) formulation.

The physical data discussed below support the proposal that all the complexes described above are based on the tetranuclear core, III, where the "in-plane" bridging species, O(3) and O(3'), may be either OH^- or OR^-. There is no evidence for any Schiff-base hydration. Given that nickel(II) and cobalt(II) in a nearly planar O_3N donor environment, such as is provided within a binuclear $[LM_2^{(II)}(OH)]$, would wish to increase their coordination number by uptake of ligands perpendicular to the O_3N plane, a second $[LM_2^{II}(OH)]$ unit would seem ideally suited to satisfy this tendency, establishing four new M–O bonds in a single association and thereby generating nucleus III. However, if the individual $[LM_2(OH)]$ units in III remained planar and adopted a separation of approximately 2 Å, appropriate for "normal" MO bonds (M = Co^{II}, Ni^{II}), the flanking aromatic nuclei would be brought into much closer contact with the neighbouring L than their van der Waals "half-thickness" (approximately 1.8 Å) would allow. In the case of $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2$, this dilemma is resolved by buckling the individual L units so that the flanking aromatic nuclei (rings A and A' in particular, Fig. 1) are bent away from the unit opposite; a



(III)

TABLE I. Vapour Pressure Osmometry, Electrical Conductance and Base Titration of 2-Methoxyethanol Solutions.

	Molecular Weights[a]		Molar Conductance (ohm^{-1} cm^2 mol^{-1})		Titration Against LiOH	
	Observed[b]	Theoretical	At 25 °C [c]	At 59 °C[c]	Number of Endpoints	Acidic (H) per L_2Ni_4
$[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$	1030 (1.46)	1076	1.4	1.8 (21.2)	1	2
			2.7	4.1 (5.3)		
	1090 (3.79)		8.2	17.2 (1.3)		
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$	1120 (2.19)	1234	1.3	2.0 (16.5)	1	2
			2.4	3.7 (4.1)		
	1230 (3.92)		6.1	13.0 (1.0)		
$[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$	1120 (2.54)	1063	4.5	5.6 (14.0)	1	2
			10.3	9.9 (3.5)		
			10.0	14.3 (0.9)		
$[LNi_2(OH)]_2(NO_3)(H)$	750 (1.91)	1019	16.9	29.4 (12.4)	1	1
			22.0	41.9 (3.1)		
	830 (2.90)		22.7	46.3 (0.8)		
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$	680 (1.72)	1212	0.8	1.2 (19.1)	1	3
			1.6	2.3 (4.8)		
	720 (3.71)		3.6	6.5 (1.2)	2[d]	1 + 2[d]
$[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$	480 (1.62)	1089	21.5	27.9 (22.1)	2	1 + 2
	510 (2.36) 590 (3.68)		32.1	46.8 (5.6)		
	660 (4.46)		35.4	56.3 (1.4)		
$NaClO_4$			34	55 (25.1)		
			39	67 (6.7)		
			42	74 (1.6)		
$NaNO_3$			27	41 (26.5)		
			32	54 (6.7)		
			36	63 (1.7)		

[a] Anhydrous complexes in 2-methoxyethanol at 59 °C. [b] Concentrations in g kg^{-1} in parentheses. [c] Concentrations at 25 °C (mol dm^{-3} × 10^4) in parentheses. [d] In methanol.

consequence of this buckling is significant lengthening of the outer two Co–O bonds [Co(2)–O(4′) and Co(2′)–O(4)] to 2.24 Å. Certain aspects of the magnetic and spectral properties of some of the complexes discussed below appear to be related to this lengthening of the "outer" M(2)–O(4′) and M(2′)–O(4) bonds in III.

Solution Measurements

In Table I are summarised results of some measurements (vapour pressure osmometry, electrical conductance and titration against hydroxide ion) on 2-methoxyethanol solutions of the nickel complexes, except for $[LNi_2OH)\cdot LNi_2(OCH_3)]_2$ and $[LNi_2(OH)\cdot LNi_2(OCH_2CH_2OCH_3)]_2$ which were insufficiently soluble. The data are generally in accord with the presence in solution either of undissociated tetranuclear formula units, *e.g.* $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$, or of charged tetranuclear species resulting from some degree of ionic dissociation, *e.g.* ionisation of the relatively poor donor ligand NO_3^- in $[LNi_2(OH)]_2(NO_3)(H)$ and ionisation of the most acidic proton in $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$ (see below).

In potentiometric titrations of the nickel complexes in 2-methoxyethanol solution against lithium hydroxide well-defined end points (Table I) consistent with the expected numbers of acidic hydrogen atoms were observed in all cases except for the pyrazole adduct whose solution behaviour was anomalous. In those examples with two titrateable hydrogens (Table I) a single end point corresponding to two protons rather than two separate end points was observed; apparently therefore the protonation sites within the tetranuclear core are spatially and electronically so well isolated that they are independent of one another. The most likely sites for these two protons are the non-bridging aminophenolic oxygen atoms, O(5) and O(5′) in III. One hydrogen atom in $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$ was much more acidic than the other two and is most likely located on the bridging phenolic oxygen atom O(8) and O(8′)

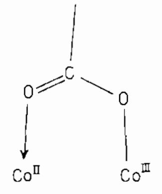
in III. The stable existence of $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$ with three protons attached to the $[LNi_2(OH)]_2$ core led us to study by titration the effect of acid upon nickel complexes with only two additional protons. Titration in 2-methoxyethanol against perchloric acid of $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$ and $[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$ showed in both cases an end point corresponding to the uptake of one proton per Ni_4 unit. However, each small addition of acid beyond the end point caused an initial sharp decrease in apparent pH followed by a slow drift to higher values, suggesting further proton consuming reactions which are probably accompanied by breakdown of the tetranuclear unit. It appears then that the tetranuclear unit can tolerate without disintegrating the addition of three protons, but no more than three. The ultimate product of proton-promoted decomposition when hydrochloric acid was used, was $(LH_4)Cl$ which could be isolated from the titration solution as scarlet crystals. The stability of the LH_4^+ cation is unusual since Schiff bases are generally very sensitive to acid promoted solvolysis yielding the protonated amine component.

Ir Spectra

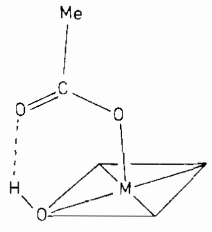
Except for some variation in the region 1340–1220 cm^{-1} and except for additional bands due to species external to the L_2M_4 unit, the ir spectra of all the proposed tetranuclear nickel(II), cobalt(II) and mixed cobalt(II)–cobalt(III) complexes were veyy similar throughout the range 4000–300 cm^{-1}, which is consistent with the common core of type III. The compounds isolated have numbers of additional protons ranging from zero to three per tetranuclear unit and the variability observed in the 1340–1220 cm^{-1} range is probably associated with differences in phenolic C–O stretching frequencies, which are expected in this region [4], arising from the different protonation patterns.

The only solvent-free compounds for which O–H stretching bands could be observed were very thoroughly dried samples of the X-ray structural material $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2 \cdot 2C_2H_5OH \cdot 2H_2O$ and of its related hydrate, both of which showed a weak but sharp band at 3565 cm^{-1}, and $[LNi_2(OH) \cdot LNi_2(OCH_3)]_2$, which showed a similar band at 3628 cm^{-1}. These absorptions are assigned to the O–H stretching frequency of the triply bridging hydroxide ion. Even for carefully dried samples of the nickel complexes carrying additional acidic protons, which must contain OH groups, no OH stretching bands could be observed; we believe these OH groups are involved in hydrogen bonding (see below).

The acetate-containing complexes showed $\gamma_{OCO(antisymm)}$, $\gamma_{OCO(symm)}$ and $\delta_{OCO(deform)}$ bands respectively as follows: nickel(II) and cobalt(II) complexes, 1554 ± 6, 1411 ± 1, 692 ± 6 cm^{-1}; mixed cobalt(II)–cobalt(III) complexes, 1565, 1410, 665 cm^{-1}. This close similarity suggests, at first sight, a common bridging function for the acetate group in all the complexes, as was established in the case of $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2 \cdot 2C_2H_5OH \cdot 2H_2O$, in which the acetate bridge was unsymmetrical, tending towards the extreme situation represented in IV. However, the acetate group in $[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2 \cdot xH_2O$ cannot be bridging for both osmometry (above) and the ir spectrum indicate that the pyridine is coordinated; pyridine bands in the ir spectrum located at 1602 (skeletal in-plane), 642 (in-plane ring deformation) and 420 cm^{-1} (out of plane deformation) are at higher frequencies than the analogous bands in the spectrum of free pyridine (1578, 604, 405 cm^{-1}) [5]. We propose, in this case, that the acetate group is unidentate as in V and that it acquires an environment not unlike that in IV by hydrogen bonding to an adjacent OH group which may be either a bridging OH^- (O(3) and O(3′) in III) or a protonated phenolic oxygen (O(5) and O(5′) in III). Unidentate acetate groups generally show $\gamma_{OCO(antisymm)}$ above 1600 cm^{-1} and $\gamma_{OCO(symm)}$ below 1400 cm^{-1}, but hydrogen bonding of the uncoordinated oxygen atom brings the two bands closer together [6] as in nickel acetate tetrahydrate [7] which is known to involve hydrogen bonded unidentate acetate and which shows $\gamma_{OCO(antisymm)}$ at 1520 cm^{-1} and $\gamma_{OCO(symm)}$ at 1413 cm^{-1}. The evidence available for the other acetate-containing nickel complexes does not definitely indicate one or other of the alternatives, IV or V, but the lack of OH stretching bands in carefully dried samples supports the latter.



(IV)



(V)

Because of the general complexity of the ir spectra it was, in some cases, impossible to locate with certainty diagnostically useful bands arising from additional species such as NO_2^- and NO_3^- and to extract any information regarding their mode of coordination.

Magnetic Properties

Magnetic susceptibilities were measured as functions of temperature over the range 300–100 °K, Curie–Weiss behaviour being observed in all cases. Weiss constants, θ, and room temperature susceptibilities and moments are recorded in Table II for both

TABLE II. Magnetic Data.

	Hydrated				Anhydrous			
	$10^6\chi_m$[a]	T(°K)	μ_{eff}(B.M.)[b]	θ(°K)[c]	$10^6\chi_m$[a]	T(°C)	μ_{eff}(B.M.)[b]	θ(°K)[c]
$[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$	4352	287	3.17	−14	4109	293	3.12	−17
$[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$	4218	283	3.10	−28	3505	287	2.85	−34
$[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$	4362	290	3.20	−8	3380	289	2.81	−12
$[LNi_2(OH)]_2(NO_3)(H)$	4484	291	3.24	−3	3304	287	2.77	−24
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$	4329	289	3.18	−12	4502	287	3.23	−17
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$	4409	289	3.21	−10	4403	298	3.25	−13
$[LNi_2(OH)\cdot LNi_2(OCH_3)]_2$	4263	293	3.17	−7	4339	293	3.20	−7
$[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2$	9835	293	4.82	−5	9380	294	4.71	−14
$[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2\cdot 2H_2O$	5520	287	3.58	−13				

[a] χ_m = molar susceptibility per metal centre, assuming all metal centres equivalent. Units cm^3 $g\text{-}atom^{-1}$. Corrected for diamagnetic contributions estimated from Pascal's constants. [b] μ_{eff} = effective magnetic moment per metal calculated from $\mu_{eff} = 2.84 (\chi_m T)^{1/2}$. [c] θ = the Weiss constant obtained from the intercept on the T axis of the linear plot of $^1/\chi_m$ *versus* T assuming $\chi_m = c/T - \theta$.

hydrated and anhydrous solids. Upon dehydration the susceptibilities of three of the nickel complexes, *viz.* $[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$, $[LNi_2(OH)]_2(CH_2CO_2)(Cl)_2(H)_3$ and $[LNi_2(OH)]_2(NO_3)(H)$, fall by *ca.* 25% indicating that one nickel atom in each tetranuclear unit acquires a low-spin configuration. Corresponding changes in the electronic spectra, discussed below, are consistent with this interpretation.

The magnetic properties of $[LCo_2^{II}(OH)]_2(CH_3CO_2)_2(H)_2$ in both hydrated and anhydrous forms are consistent with all four cobalt centres having the high spin configuration, although the electronic spectra, discussed below, suggest that the environment of one or more of the cobalt centres changes from pseudo-octahedral to square pyramidal upon dehydration.

Both the magnetic properties of $[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2\cdot 2H_2O$ and the dioxygen consumed in its formation indicate the presence of equal numbers of cobalt(II) and cobalt(III). On the assumption that the cobalt(III) centres are low spin and diamagnetic the observed susceptibilities imply moments of 4.86 B.M. (at 96 °K) to 5.06 B.M. (at 287 °K) per cobalt(II) centre, which are normal for high spin cobalt(II). The magnetic properties of $[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 2H_2O$ were measured at room temperature only, but the moment of 3.51 B.M. per cobalt (averaged over all cobalt present) is in close agreement with 3.58 B.M. per cobalt observed for $[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2\cdot 2H_2O$.

Electronic Spectra

The evidence discussed below suggests that in 2-methoxyethanol and in the undried solids ligand atoms occupy all four of the axial coordination positions represented as vacant in III, thereby providing each metal centre with a pseudo-octahedral environment. Even if all four additional donors were identical, two distinctly different octahedral environments would be provided by III and this difference would be exaggerated by the stretching of the outer M(2)–O(4′) and M(2′)–O(4) bonds. In the nickel(II) and cobalt(II) complexes isolated, however, the situation is further complicated by the fact that at least two different donors occupy the axial positions and also by the fact that varying numbers of protons are attached to the phenolate donor atoms. The evidence below also indicates that in some cases axial water ligands may be removed under vacuum from the tetranuclear core yielding square pyramidal centres which may, in the case of nickel(II), be of either high spin or low spin configuration depending presumably on the extent of stretching of the remaining bond axial to the O_3N donor set of a binucleating unit.

Band maxima observed for 2-methoxyethanol solutions and also for both hydrated and anhydrous solid samples by diffuse reflectance are presented in Table III. In both solid and solution the effective upper limit for observation of d ⟷ d bands was approximately 15000–16000 cm^{-1} where the tail of an intense absorption centred at higher energies dominated the spectra.

The solution spectra of the nickel(II) complexes except for $[LNi_2(OH)]_2(NO_3)(H)$ which underwent a slow change in solution, were relatively simple showing a band near 11000 cm^{-1} with some indication of broadening on the low energy side and with a relatively sharp shoulder near 13000 cm^{-1}. These solution spectra are consistent with all four nickel centres being effectively octahedral, the 11000 cm^{-1} band being ascribed to the lowest energy spin-allowed transition, $^3A_{2g} \rightarrow {}^3T_{2g}$, and the shoulder near 13000 cm^{-1} being ascribed to the spin-forbidden, $^3A_{2g} \rightarrow {}^1E_g$ transition frequently observed in octahedral nickel complexes [8]. Undoubtedly the band observed is a composite, arising from different sorts

TABLE III. Electronic Spectra.

Complex	State[a]	γ_{max} ($cm^{-1} \times 10^{-3}$)					ϵ_{max} (solution) ($dm^3\ mol^{-1}\ cm^{-1}$)
$[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$	S (2.12×10^{-3})				11.4	13.2(sh)	56
	DRH		8.7 sh		11.5	13.3 sh	
	DRA	5.9			11.6	13.2 sh	
$[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$	S (1.40×10^{-3})				11.5	13.1 sh	57
	DRH		8.7 sh		11.5	13.3 sh	
	DRA	6.0 sh			12.2 sh		
$[LNi_2(OH)]_2(NO_3)(H)$	S[b] (1.84×10^{-2})		8.2 sh	9.5	11.5	13.2 sh	37 (11.5 band); 41 (9.5 band)
	DRH		8.3 sh		10.6	13.5 sh	
	DRA	6.0 sh			12.3 sh		
$[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$	S (2.21×10^{-3})				11.6	13.2 sh	58
	DRH		8.7 sh		11.6	13.2 sh	
	DRA	5.7			11.8		
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$	S (1.91×10^{-3})				11.3	13.0 sh	57
	DRH		9.1 sh		10.8	12.9 sh	
	DRA				10.8	12.9 sh	
$[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$	S (1.65×10^{-3})				11.4	13.0 sh	61
	DRH	7.1 sh	9.1 sh		11.2	13.0 sh	
	DRA	6.3			11.4	12.9 sh	
$[LNi_2(OH) \cdot LNi_2(OCH_3)]_2$	DRH	5.9			10.9		
	DRA	5.9			11.1		
$[LCo_2(OH)](CH_3CO_2)_2(H)_2$	DRH				10.0		
	DRA	4.4			9.5		

[a] S = solution in 2-methoxyethanol: solution concentrations in mol dm^{-3} in parentheses. DRH = diffuse reflectance of solid hydrate. DRA = diffuse reflectance of anhydrous solid.

[b] Spectrum of freshly prepared solution. The $9.5 \times 10^3\ cm^{-1}$ band gradually decays at room temperature and eventually the spectrum becomes similar to the other solution spectra with a maximum at $11.5 \times 10^3\ cm^{-1}$.

of pseudo-octahedral nickel present in the nucleus. The slight broadening on the lower energy side may result from the presence of more than one octahedral nickel environment and also from the asymmetry [8] associated with the elongation of bonds M(2)–O(4′) and M(2′)–O(4) in III.

The diffuse reflectance spectra of the solid hydrated nickel complexes are characterised, like the solution spectra, by a band near 11000 cm^{-1}, presumably with a similar combination of origins, but the broadening on the low energy side is much more pronounced. In a number of cases discernible shoulders are apparent, generally in the 8200–9500 cm^{-1} range but as low as 7100 cm^{-1} in the pyridine adduct (Table III).

In several cases marked changes in the diffuse reflectance spectra accompany vacuum drying of the solids. The three compounds $[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$, $[LNi_2(OH)]_2(NO_3)(H)$ and $[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$, which upon drying become less paramagnetic to an extent consistent with spin pairing on one out of four nickels, exhibit spectral changes shown by none of the other compounds, namely, a very marked increase in absorption in the 13000–18000 cm^{-1} region so that the 11000 cm^{-1} band becomes apparent only as a shoulder. We propose in these three cases that dehydration removes a coordinated water molecule from one nickel centre leaving its environment roughly square pyramidal with the axial Ni–O bond (M(2)–O(4′) or M(2′)–O(4) in III) elongated to such an extent that spin pairing occurs [9]. Other established examples of approximately square pyramidal low-spin nickel(II) complexes with four relatively strong bonds in the pyramidal base and a weak bond on the axis show their lowest energy d ⟷ d band in the 15000–20000 cm^{-1} region which is generally much more intense than the d ⟷ d bands for octahedral nickel(II) [8b, 10, 11].

In other cases dehydration apparently produces approximately square pyramidal metal centres without change in spin state. Thus, solid hydrated $[LCo_2^{II}(OH)]_2(CH_3CO_2)_2(H)_2$ shows a "single" d ⟷ d band at 10000 cm^{-1}, which is consistent with pseudo-octahedral stereochemistry about high-spin cobalt(II) [8a], whereas, after dehydration, a new band appears at 4400 cm^{-1} and the remnant of the octahedral band is somewhat broadened and slightly shifted to 9500 cm^{-1}. The new band is strongly suggestive of five-coordinate cobalt(II) [8a, 12] and can be compared with a d ⟷ d band at 4500 cm^{-1} in the reflectance spectrum of high spin β-Co(paphy)Cl_2 (paphy = 1,3-bis(2′-pyridyl)-2,3-diaza-1-propene) which has an established approximately square pyramidal metal environment [13]. The diffuse reflectance spectrum of hydrated $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$ undergoes a change upon dehydration of the solid similar to that observed for the cobalt analogue; in addition to the initial "octahedral" band at 11500 cm^{-1}, a new band appears after dehydration, at 5900 cm^{-1} which appears much too low in energy to originate from pseudo-octahedral nickel(II) and which can be assigned to the lowest energy d ⟷ d transition of high spin nickel(II) in an approximately square pyramidal environment ($^3B_1 \rightarrow {}^3E(F)$) [12]. The implication of the electronic spectral changes accompanying dehydration of this pair of analogous nickel(II) and cobalt(II) complexes, namely, that acetate ions and water molecules occupy the axial sites of III and removal of the latter generates roughly square-pyramidal metal centres, is consistent with the non-bridging role for the acetate groups proposed above.

For the three nickel complexes in which one out of four nickel centres becomes diamagnetic upon dehydration, a new band (evident only as a shoulder) in the range 5700–6000 cm^{-1} also appears, which implies that both high spin and low spin square pyramidal nickel environments are generated in these cases. Presumably the two types of square pyramidal nickel environment differ in the degree of axial stretching.

The spectra of both hydrated and anhydrous $[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$ are virtually identical as is consistent with the occupation of the four axial positions by two monodentate acetates and two neutral pyrazole units. However, the significant spectral changes accompanying dehydration of hydrated $[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$ (Table III) are difficult to rationalise for analytical data indicate no loss of pyridine.

$[LNi_2(OH)\cdot LNi_2(OCH_3)]_2$ was outstanding in showing a clearly defined band at 5900 cm^{-1} ascribed to square pyramidal nickel(II), not only in the anhydrous form but also in the hydrate. For this compound and the related $[LNi_2(OH)\cdot LNi_2(OCH_2CH_2OCH_3)]_2$ we propose an octanuclear arrangement, represented in Figure 2, which consists of two tetranuclear units of type III linked together by two

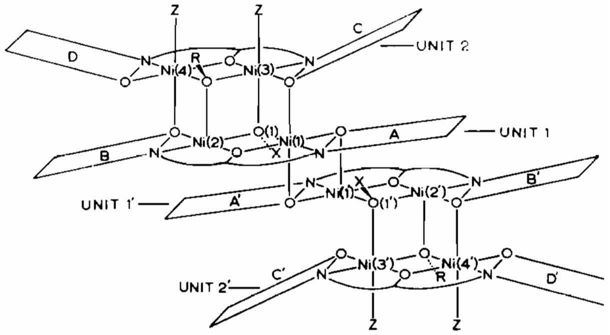


Figure 2. Proposed octanuclear structure for $[LNi_2(OH)\cdot LNi_2(OR)]_2$ (R = CH_3 or $CH_2CH_2OCH_3$). The approximately planar units designated A, B, C, D, A′ *etc.* represent the *o*-iminophenolic groups of the L units.

tetranuclear units of type III linked together by two new Ni–O bonds involving the phenolic oxygen atoms, O(5) and O(5′), of III which were non-bridging prior to formation of the two new bonds. An almost identical mode of association (but between binuclear rather than tetranuclear units) has been observed in a crystallographic study of the related complex $[LCu_2(C_3H_3N_2)]_2$ [14] (where $C_3H_3N_2^-$ is a pyrazolate anion occupying the "in-plane" bridging site). Both molecular models and the crystal structure determination of $[LCu_2(C_3H_3N_2)]_2$ [14] indicate that, as a result of the Ni–O bonds between units 1 and 1′ the aromatic systems A and A′ render coordination at the vacant sites above Ni(2′) and below Ni(2) impossible. Thus the model accounts for the presence of square pyramidal nickel(II) even in the hydrated form. The model also accounts for the otherwise puzzling appearance of one hydroxide and one alkoxide per four nickel centres, for ring A of unit 1 sterically prevents the incorporation of anything larger than OH at the bridging site of unit 1′(O(1′)–X); the same argument also applies to the interaction between O(1)–X of unit 1 and system A′ of unit 1′. However, the same constraints do not apply to the bridging sites of units 2 and 2′ which could reasonably accommodate alkoxy bridges. $[LNi_2(OH)\cdot LNi_2(OCH_3)]_2$ in the hydrated form shows an "octahedral" band at 10900 cm^{-1} and a significantly less intense "square pyramidal" band at 5900 cm^{-1}, whereas, after dehydration, the relative intensities are reversed. In terms of the model represented in Figure 2 this observation is readily interpreted; in the hydrated form sites Z are presumed occupied by water molecules yielding, in all, six octahedral and two square pyramidal nickel centres whereas, after dehydration, the sites Z are vacant leaving six square pyramidal and two octahedral nickel centres.

Experimental

4-Hydroxy-3,5-toluenedicarbaldehyde was prepared by the method described by Ullmann and Brittner [15].

2-Hydroxy-5-methylisophthalaldehyde di-2′-hydroxyanil (LH₃) was prepared as reported previously [1].

$[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$

A solution of 2-aminophenol (0.85 g, 8.0 mmol) and 4-hydroxy-3,5-toluenedicarbaldehyde (0.66 g, 4.0 mmol) in methanol (40 ml) was heated at the boiling point for ten minutes and then added to a cold solution of nickel acetate tetrahydrate (1.99 g, 8.0 mmol) in methanol (25 ml). The mixture was gently agitated until all solid LH_3 had dissolved (hastened by gentle warming if necessary) and filtered. The brown filtrate was heated at boiling point on the water bath for three or four minutes, after which time brown crystals appeared. These were collected from the hot suspension and were washed with chilled methanol (2 × 2 ml). The undried complex was taken up with stirring in warm ethylacetate (*ca.* 170 ml per 1.5 g complex) and after about thirty seconds, before complete dissolution of the complex had occurred, the mixture was filtered. The dark brown filtrate rapidly yielded fine orange-brown crystals, which were collected and washed with chilled ethylacetate. The product was dried under vacuum at 110 °C for two hours to a brown powder and then exposed to the atmosphere. *Anal.* Calcd. for $C_{46}H_{50}N_4O_{17}Ni_4$ $\{[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2\cdot 5H_2O\}$: C, 47.4; H, 4.3; N, 4.8; Ni, 20.1. Found: C, 47.2; H, 4.7; N, 4.7; Ni, 20.2.

$[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2$

A cold solution of cobalt acetate tetrahydrate (4.98 g, 20 mmol) in methanol (50 ml) under dinitrogen, was quickly added in one lot to a suspension of LH_3 (3.64 g, 10.0 mmol) in methanol (80 ml). The mixture was warmed gently to hasten dissolution of LH_3 and filtered. After a period of about five minutes near boiling temperature on the water bath, the filtrate yielded red-brown crystals which were quickly collected, washed with ice-cold methanol (5 ml), dried under vacuum at room temperature and then exposed to the atmosphere. *Anal.* Calcd. for $C_{46}H_{56}N_4O_{20}Co_4$ $\{[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2\cdot 8H_2O\}$: C, 45.3; H, 4.6; N, 4.6; Co, 19.3. Found: C, 45.5, H, 4.6; N, 4.6; Co, 18.9.

$[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2$

A cold solution of 2-aminophenol (1.09 g, 10.0 mmol) and 4-hydroxy-3,5-toluenedicarbaldehyde (0.82 g, 5.0 mmol) in methanol, was added to nickel acetate tetrahydrate (2.45 g, 10.0 mmol) in methanol (30 ml). After the addition of a solution of pyrazole (1.36 g, 20.0 mmol) in methanol (14 ml), the mixture was filtered and heated at boiling temperature for five minutes. The resulting brown crystals were collected, washed with small quantities of chilled methanol, dried at 110 °C under vacuum and then exposed to the atmosphere. *Anal.* Calcd. for $C_{52}H_{52}N_8O_{14}Ni_4$ $\{[LNi_2(OH)]_2(CH_3CO_2)_2(C_3H_4N_2)_2(H)_2\cdot 2H_2O\}$: C, 50.1; H, 4.2; N, 9.0; Ni, 18.8. Found: C, 50.3; H, 3.9; N, 8.7; Ni, 18.7.

$[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2$

Method (a): The preparation followed that of the pyrazole complex above, except that the solution of pyrazole was replaced with pyridine (4 ml, 50 mmol). The red–brown product was solvated with pyridine and it was necessary to dry at 130 °C under vacuum for 16 hours to remove all lattice pyridine.

Drying caused the complex to turn almost black, but the red–brown colour was restored on exposure to the atmosphere.

Method (b): Pyridine (0.11 g, 1.4 mmol) was added to a cold suspension of hydrated $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$ (0.19 g, *ca.* 0.32 mmol) in methanol (15 ml) to give a deep red–brown solution. After being filtered, the solution was set aside in a stoppered flask for one day. The resulting crystals were collected, washed with chilled methanol, dried at 130 °C under vacuum for 16 hours and then exposed to the atmosphere. *Anal.* Calcd. for $C_{56}H_{54}N_6O_{14}Ni_4$ $\{[LNi_2(OH)]_2(CH_3CO_2)_2(C_5H_5N)_2(H)_2\cdot 2H_2O\}$: C, 53.0; H, 4.3; N, 6.6; Ni, 18.5. Found: C, 53.0; H, 4.4; N, 6.9; Ni, 18.8.

$[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3$

A cold solution of 4-hydroxy-3,5-toluenedicarbaldehyde (0.32 g, 2.0 mmol) and 2-aminophenol (0.43 g, 4.0 mmol) in methanol (20 ml), was added to nickel acetate tetrahydrate (0.76 g, 1.5 mmol) and nickel chloride hexahydrate (0.71 g, 1.5 mmol) in methanol (14 ml). The mixture was filtered, heated at boiling point for five minutes and set aside in a stoppered flask for two days. The crystals which separated were washed with ice-cold methanol, dried under vacuum at 80 °C and then exposed to the atmosphere. *Anal.* Calcd. for $C_{44}H_{54}Cl_2N_4O_{18}Ni_4$ $\{[LNi_2(OH)]_2(CH_3CO_2)(Cl)_2(H)_3\cdot 8H_2O\}$: C, 42.9; H, 4.4; N, 4.6; Cl, 5.8; Ni, 19.1. Found C, 43.2; H, 4.3; N, 4.4; Cl, 5.8; Ni, 18.9.

$[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$

A warm solution of sodium nitrite (0.10 g, 1.4 mmol) in methanol (50 ml) was filtered into a previously filtered, warm solution of hydrated $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$ (0.28 g, *ca.* 0.47 mmol) in methanol (130 ml). Over a period of five minutes during which the mixture was stirred, fine yellow–ochre crystals separated. These were collected and washed with methanol (2 × 5 ml), and dried at 80 °C under vacuum to a red–brown powder. On re-exposure to the atmosphere, the product became lighter in colour. *Anal.* Calcd. for $C_{44}H_{47}N_5O_{17}Ni_4$ $\{[LNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2\cdot 5H_2O\}$: C, 45.8; H, 4.1; N, 6.1; Ni, 20.4. Found: C, 45.5, H, 4.2; N, 5.7; Ni, 20.6.

$[LNi_2(OH)]_2(NO_3)(H)$

Warm solutions of nickel nitrate hexahydrate (29.1 g, 100 mmol) in methanol (20 ml) and sodium *n*-butyrate (11.0 g, 100 mmol) in methanol (60 ml), were mixed and the resulting white precipitate of sodium nitrate filtered off and discarded. The green filtrate was reduced to 20 ml in volume on the water bath, cooled, and the separate more mobile liquid phase which formed was discarded. The very viscous phase was heated at 60 °C under water-pump pressure for 15 minutes and the brittle residue obtained on cooling was taken up in acetonitrile (16 ml). The green solution was filtered and evaporated to dryness at 60 °C, firstly at the water pump, then using the oil pump. The green brittle residue had the composition $Ni(C_4H_8O_2)(C_4H_7O_2)(NO_3)\cdot 3H_2O$. *Anal.* Calcd. for $C_8H_{21}O_{10}N$ Ni: C, 27.5; H, 5.8; N, 4.0. Found: C, 27.7; H, 5.3; N, 3.9.

A warm solution of the butyrate/nitrate salt (2.7 g, *ca.* 6 mmol) in acetonitrile (7 ml) was added to a suspension of LH_3 (1.04 g, 3.0 mmol) in warm acetonitrile (18 ml) and the resulting solution was filtered. Water (3 ml) was added to the filtrate, and the mixture was heated for about five minutes at boiling point yielding brown crystals. These were collected, washed with chilled acetonitrile (3 × 1 ml), dried at 80 °C under vacuum to a red–brown powder and then exposed to the atmosphere. *Anal.* Calcd. for $C_{42}H_{39}N_5O_{14}Ni_4$ $\{[LNi_2(OH)]_2(NO_3)(H)\cdot 3H_2O\}$: C, 47.0; H, 3.8; N, 6.5; Ni, 21.9. Found: C, 47.0; H, 3.9; N, 6.7; Ni, 22.1.

$[LNi_2(OH)\cdot LNi_2(OR)]_2$ (R = CH_3 or $CH_2CH_2OCH_3$)

These complexes appeared as fine brown crystalline precipitates as the endpoint was approached during the potentiometric titrations of solutions of acidic nickel(II) complexes in methanol or 2-methoxyethanol, against a solution of lithium hydroxide monohydrate in the same solvent. The products were collected, washed with the titration solvent, dried at 125 °C under vacuum and then exposed to the atmosphere. *Anal.* Calcd. for $C_{90}H_{88}N_8O_{24}Ni_8$ $\{[LNi_2(OH)\cdot LNi_2(C_3H_7O_2)]_2\cdot 6H_2O\}$: C, 50.6; H, 4.2; N, 5.2; Ni, 22.0. Found: C, 50.8; H, 3.9; N, 4.9; Ni, 22.1. Calcd. for $C_{86}H_{78}N_8O_{21}Ni_8$ $\{[LNi_2(OH)\cdot LNi_2(OCH_3)]_2\cdot 5H_2O\}$: C, 50.9; H, 3.9; N, 5.5; Ni, 23.1. Found: C, 50.7; H, 4.0; N, 5.4; Ni, 23.6.

$(LH_4)Cl\cdot 4^1/_3H_2O$

This compound was isolated from the solution obtained at the completion of the potentiometric titration of a solution of $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$ (0.20 g) in methanol (50 ml), against a methanol solution of hydrochloric acid (*ca.* 0.15 mol dm^{-3}) prepared from the concentrated aqueous reagent. Slow evaporation of the solution, then containing approximately five-fold molar excess of hydrochloric acid, to half volume was accompanied by the separation of scarlet needles. These were collected, washed with chilled methanol and dried in air. *Anal.* Calcd. for $C_{21}H_{27.7}ClN_2O_{7.3}$: C, 54.7; H, 6.1; N, 6.1; Cl, 7.7. Found: C, 54.8; H, 5.8; N, 6.1; Cl, 7.7.

$[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2$

Hydrated $[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2$ (2.5 g) was taken up in hot methanol (1.75 litre) under a nitrogen atmosphere. After refluxing for five minutes, the mixture was filtered free of any undissolved solid (under dinitrogen) and a steady stream of dioxygen was bubbled through the initially clear, orange–red filtrate, for thirty minutes, during which time the solution darkened and yielded black plates. These were collected and were washed with methanol. The freshly isolated complex was solvated and efflorescent. The solid (2.1 g) was dried at 110 °C under vacuum and was then exposed to the atmosphere. *Anal.* Calcd. for $C_{48}H_{46}N_4O_{14}Co_4$ $\{[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2\cdot 2H_2O\}$: C, 50.6; H, 4.1; N, 4.9; Co, 20.7. Found: C, 50.3; H, 4.1; N, 5.3; Co, 20.6.

$[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2$

The complex could be prepared by two methods.

Method (a): A solution of hydrated $[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2$ (0.53 g) in boiling ethanol (40 ml) was filtered and set aside for three days in an open vessel. The volume of the solution was not allowed to drop below 30 ml. There was no need to employ oxygen-free conditions as in the previously described preparation. The efflorescent black crystals (deep red by transmitted light) were collected, washed with ethanol and dried in vacuum at room temperature. *Anal.* Calcd. for $C_{46}H_{41}N_4O_{13.5}Co_4$ $\{[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 1.5H_2O\}$: C, 49.0; H, 3.9; N, 5.0; Co, 20.8; Found: C, 49.0; H, 3.8; N, 5.1; Co, 20.9.

Method (b): The methoxo complex $[LCo^{II}Co^{III}(OCH_3)]_2(CH_3CO_2)_2\cdot 2H_2O$ (0.35 g) was suspended in refluxing ethanol containing approximately 4% water (150 ml) for fifteen minutes. The mixture was filtered and the filtrate transferred to an open crystallizing dish. The dish was placed in a sealed container (glove bag) through which dry air was passed until the volume of liquid was reduced by one half. The resulting, efflorescent black crystals were collected and dried at room temperature under vacuum. *Anal.* Calcd for $C_{46}H_{45}N_4O_{15.5}Co_4$ $\{[LCo^{II}Co^{III}(OH)]_2(CH_3CO_2)_2\cdot 3.5H_2O\}$: C, 46.0; H, 4.4; N, 4.7; Co, 19.6. Found: C, 46.3; H, 4.3; N, 4.6; Co, 19.5.

Dioxygen Uptake by $[LCo_2^{II}(OH)]_2(CH_3CO_2)_2(H)_2$

The relative insolubility of $[LCo_2(OH)]_2(CH_3CO_2)_2(H)_2$ in even the best solvent, methanol, presented serious difficulties in the measurement of its consumption of dioxygen. Direct volumetric measurement of dioxygen uptake by homogeneous saturated solutions would involve unacceptably large errors because the volume of dioxygen consumed would be a minute fraction of the total volume of the solution. Measurements therefore were made upon suspensions, the suspended starting material being gradually replaced by suspended product. It was found necessary, under these circumstances, to conduct the oxygenation at as elevated a temperature as possible, in order to achieve complete or nearly complete reaction in a reasonable time. Reactions were conducted at 50 °C under pure dioxygen at atmospheric pressure in a 500 ml reaction vessel fitted with an efficient magnetic stirrer and connected to a gas burette containing dioxygen-saturated methanol. The whole system was equilibrated to 25 °C before and after the reaction at 50 °C so that the volume absorbed could be measured. In a typical run only approx. 5 ml dioxygen at atmospheric pressure were absorbed by approx. 0.5 g of cobalt(II) complex suspended in approx. 350 ml methanol and the error in the volume change was estimated at approx. ±7%.

Physical Methods and Instrumentation

Potentiometric titrations. Base titrations of solutions of the complexes (0.15 g to 0.20 g) in 2-methoxyethanol or methanol (~50 ml), were against solutions of lithium hydroxide monohydrate (~0.08 *M*) standardized with potassium hydrogen phthalate. Acid titrations of the complexes were against solutions of perchloric acid in 2-methoxy-ethanol (*ca.* 0.13 mol dm^{-3}). In one case, that of $[LNi_2(OH)]_2(CH_3CO_2)_2(H)_2$, a solution of hydrochloric acid (*ca.* 0.16 mol dm^{-3}) in methanol, was also used. Acid solutions were prepared from the concentrated aqueous reagents (A.R.) by dilution. They were standardized potentiometrically against a solution of recrystallized tris-(hydroxymethyl)aminomethane. All titrations were followed potentiometrically using glass and calomel electrodes connected to an E.I.L. Model 23A direct-reading potentiometer.

Spectra. Infra-red spectra were measured on samples prepared as pressed KBr discs, and nujol and hexachlorobutadiene mulls, using either a Perkin–Elmer 421 spectrophotometer or a Unicam SP. 1200 grating infra-red spectrophotometer. All spectra of anhydrous complexes were on samples prepared as mulls in a dry-box or glove-bag. Diffuse reflectance spectra were obtained from a Beckman DK-2A ratio recording spectrophotometer used with a Beckman reflectance attachment. A barium sulphate reference surface was employed. Solution spectra were recorded on a Hitachi E.P.S.-3T spectrophotometer using 1 cm and 5 cm optical silica cells.

Magnetic measurements. Magnetic measurements over a temperature range were made by the Gouy method. The field was calibrated before each run using $HgCo(CNS)_4$. All samples were packed in a flat-bottomed silica tube and for anhydrous samples, this was done in a dry box.

Electrical conductivity. The measurements were made using a Phillips PR9500 conductivity measuring bridge and a conductivity cell fitted with platinum black electrodes. The solutions were kept at constant temperature in thermostated water baths. When measurements were made at two different temperatures, concentrations were corrected for density changes.

Molecular weight determinations. Molecular weights were determined with a Perkin–Elmer Model 115 vapour-pressure osmometer. The apparatus was calibrated with solutions of benzil in 2-methoxyethanol (at 58.9 °C). The solvent was purified by refluxing over molecular sieves (Union Carbide Molecular Sieves, Type 3A) followed by fractional distillation and was stored under dry nitrogen and transferred using syringe techniques. All complexes were dried at 110 °C under vacuum for one hour before the solutions were prepared in a moisture-free atmosphere.

Analytical methods. All analyses were done on samples equilibrated in the atmosphere. Carbon, hydrogen, nitrogen, chloride and metal (by ash) were determined by the Australian Microanalytical Service, Division of Applied Chemistry, C.S.I.R.O., Melbourne.

Acknowledgments

D. G. V. thanks the University of Melbourne for a Commonwealth Postgraduate Research Award. R. R. is grateful to the Australian Research Grants Committee for providing the Perkin–Elmer Model 115 vapour-pressure osmometer.

References

1 R. Robson, *Aust. J. Chem., 23,* 2217 (1970).

2 W. D. McFadyen, R. Robson and H. Schaap, *Inorg. Chem., 11,* 1777 (1972).

3 B. F. Hoskins, R. Robson and D. Vince, *Chem. Comm.,* 392 (1973).

4 B. D. Sarma, K. R. Ray, R. E. Sievers and J. C. Bailar, *J. Am. Chem. Soc., 86,* 14 (1964); B. D. Sarma and J. C. Bailar, *J. Am. Chem. Soc., 77,* 5476 (1955); C. S. Marvel, S. A. Aspey and E. A. Dudley, *J. Am. Chem. Soc., 78,* 4905 (1956).

5 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965); N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. A. Sharpe, *J. Inorg. Nucl. Chem., 18,* 79 (1961).

6 C. Oldham, *Prog. Inorg. Chem., 10,* 223 (1968).

7 N. F. Curtis, *J. Chem. Soc. A,* 1579 (1968).

8 a) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier (1968). b) L. Sacconi, "Transition Metal Chemistry", 4, 199 (1968).

9 L. Sacconi, *Coord. Chem. Rev., 8,* 351 (1972).

10 P. Dapporto, R. Morassi and L. Sacconi, *J. Chem. Soc. A,* 1298 (1970).

11 A. Bianci and C. A. Ghilardi, *J. Chem. Soc. A,* 1096 (1971).

12 R. Morassi, I. Bertini and L. Sacconi, *Coord. Chem. Rev., 11,* 343 (1973).

13 I. G. Dance, M. Gerloch, J. Lewis, F. S. Stephens and F. Lions, *Nature, 210,* 298 (1966).

14 D. G. Vince, *Ph. D. Thesis,* University of Melbourne.

15 F. Ullman and K. Brittner, *Ber., 2,* 2539 (1909).