Synthesis and Magnetic Properties of Binuclear Complexes of Unidentate Ligands with Acetylacetonates of Bivalent Manganese, Cobalt, and Nickel

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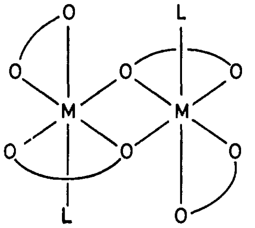
The magnetic properties of the binuclear complexes $[M_2L(acac)_4]$ [M = Mn, L = dimethylformamide (dmf); M = Co or Ni, L = pyridine (py); acac = acetylacetonate] and $[M_2L_2(acac)_4]$ [M = Mn, L = allylamine; M = Co, L = cyclohexylamine; M = Ni, L = piperidine (pip)] have been studied in the range 4—300 K. The complex $[Ni_2(py)(acac)_4]$ is ferromagnetic but $[Ni_2(pip)_2(acac)_4]$ is antiferromagnetic. The cobalt and manganese compounds have magnetic moments similar to those of monomeric octahedral complexes. The results are interpreted in terms of current theories of magnetic exchange, and related to the structures of the complexes. The preparation and characterization of the new complexes $[Ni_2(3Me\text{-}py)(acac)_4]$ (3Me-py = 3-methylpyridine), $[Ni_2(4Me\text{-}py)(acac)_4]$, $[Ni_2\{N(C_6H_{11})H_2\}_2(acac)_4]$, and $[M_2(NPhH_2)_2(acac)_4]$ (M = Co or Ni) are described.

THE earliest interpretation[1] of magnetochemical results for polynuclear co-ordination compounds introduced the parameter J, whose sign and magnitude described the deviation of the data from those for monomeric compounds. Very many later studies have yielded empirical parameters for a large number of polynuclear complexes, but only recently have these been incorporated in molecular-orbital[2] or angular-overlap[3] approaches which can cover a large number of compounds. In most non-diamagnetic polynuclear complexes the metal–metal separation is too great for direct spin coupling and the magnetic interaction is transmitted through the ligands by the so-called ' superexchange ' mechanism. The most important structural feature which determines the extent of superexchange is usually the MXM angle, where X is the bridging atom. This result was first found for metal oxides and other lattice structures[4] but has since been applied to co-ordination compounds,[5] proving particularly effective in oxo- or hydroxo-bridged copper(II) dimers.[6] However, in drawing comparisons over many compounds, other variable features in the structures become important, such as the role of the non-bridging ligands and changes in the stereochemistry at the metal atoms.[3b]

Most of the comparisons between structure and magnetism have concerned copper(II) complexes, as few of the complexes can be prepared for other metals. We have therefore prepared a group of complexes $[M_2L_n(acac)_4]$, where M is Mn, Co, or Ni, L is a unidentate ligand, acac = acetylacetonate, and n is 1 or 2. With these compounds we have examined the effect on magnetic properties of changing only the metal ion in an otherwise invariant structure. Moreover, by comparing a pair of compounds of the same metal but having different values of n we have extended comparisons of magnetic data with the MXM bridging angle, since this is quite different in the two structures.

In the preceding paper[7] we described the crystal and molecular structures of $[M_2(py)(acac)_4]$ (M = Co or Ni, py = pyridine) and of $[Ni_2(pip)_2(acac)_4]$ (pip = piperidine). Previous workers have determined the molecular structures of $[Mn_2(all)_2(acac)_4]$ (all = allylamine)[8] and $[Co_2(cy)_2(acac)_4]$ (cy = cyclohexylamine).[9] The only member of our group of complexes which has not been crystallographically established is $[Mn_2L(acac)_4]$, but a report[10] of $[Mn_2(dmf)(acac)_4]$ (dmf = dimethylformamide) suggests that this complex will fill the gap. In this report, i.r. evidence is used to deduce a structure containing a hitherto unknown bridging role for the oxygen of the dmf, but bridging acac units are more likely and also satisfy the i.r. spectrum.



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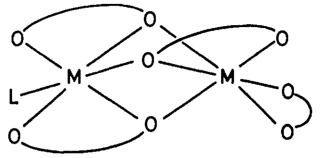

II.

Complexes having the formula $[M_2L_2(acac)_4]$ possess structures in which oxygen atoms from two acac ligands form monoatomic bridges between the metal atoms, structure (I), so that the two MLO_5 octahedra share an edge. Complexes having the formula $[M_2L(acac)_4]$ have three bridging oxygen atoms so that MO_6 and MLO_5 octahedra share a face, structure (II).

This paper describes the magnetic properties of these compounds and also describes the preparation and characterization of the new complexes $[Ni_2(4Me\text{-}py)(acac)_4]$ (4Me-py = 4-methylpyridine), $[M_2(3Me\text{-}py)(acac)_4]$, $[Ni_2(cy)_2(acac)_4]$, $[M_2(pip)_2(acac)_4]$, and $[M_2(NPhH_2)_2(acac)_4]$ (M = Co or Ni).

EXPERIMENTAL

Preparations.—Only the manganese compounds are unstable to oxygen but all the complexes are sensitive to hydrolysis to some extent. Dried reagents and apparatus were used with usual vacuum-line and glove-box methods.

Hexakis(pentane-2,4-dionato)trinickel(II). Diaquabis(pentane-2,4-dionato)nickel(II)[11] was sublimed at 140 °C at a pressure of 10^{-4} mmHg * to yield the green anhydrous $[Ni_3(acac)_6]$. This was stored in a vacuum desiccator if not used immediately after sublimation.

*Tetrakis(pentane-*2,4-*dionato)(pyridine)dinickel*(II). A method was adapted from that of Fackler.[12] The complex $[Ni_3(acac)_6]$ (6.49 g) was dissolved in benzene (20 cm^3) and pyridine (1 cm^3) was added. The solvent and any excess of base were removed under vacuum. The green $[Ni_2(py)(acac)_4]$ was recrystallized from light petroleum (b.p. 100—120 °C) and dried over $CaCl_2$ *in vacuo*, yield 4.7 g (63%), m.p. 184—187 °C (Found: C, 50.2; H, 5.5; N, 2.3; Ni, 18.6. Calc. for $C_{25}H_{33}NNi_2O_8$: C, 50.6; H, 5.6; N, 2.4; Ni, 18.5%).

(4-*Methylpyridine)tetrakis(pentane-*2,4-*dionato)dinickel*(II). The complex $[Ni_2(4Me\text{-}py)(acac)_4]$ was prepared in the same way as $[Ni_2(py)(acac)_4]$ using $[Ni_3(acac)_6]$ (8.28 g) and 4-methylpyridine (1.6 cm^3), yield 3.6 g (37%), m.p. 177—180 °C (Found: C, 52.4; H, 5.8; N, 2.2; Ni, 18.9. Calc. for $C_{26}H_{35}NNi_2O_8$: C, 51.5; H, 5.9; N, 2.3; Ni, 19.3%).

(3-*Methylpyridine)tetrakis(pentane-*2,4-*dionato)dinickel*(II). The complex $[Ni_2(3Me\text{-}py)(acac)_4]$ was prepared in the same way as the two previous compounds using the same quantities as for $[Ni_2(4Me\text{-}py)(acac)_4]$, yield 6.5 g (66%), m.p. 170—174 °C (Found: C, 52.4; H, 5.9; N, 2.5; Ni, 19.0. Calc. for $C_{26}H_{35}NNi_2O_8$: C, 51.5; H, 5.9; N, 2.3; Ni, 19.3%).

*Bis(cyclohexylamine)tetrakis(pentane-*2,4-*dionato)dinickel*(II). The complex $[Ni_2(cy)_2(acac)_4]$ was prepared by either of the published methods for the cobalt analogue [13] and purified by recrystallization from benzene or by sublimation at 100 °C and 10^{-4} mmHg, but the pale blue complex became green on prolonged heating, probably decomposing to $[Ni_3(acac)_6]$, yield 69% (Found: C, 53.9; H, 7.7; N, 3.8; Ni, 16.4. Calc. for $C_{16}H_{27}NNiO_4$: C, 54.1; H, 7.6; N, 3.9; Ni, 16.5%).

*Tetrakis(pentane-*2,4-*dionato)dipiperidinedinickel*(II). The complex $[Ni_3(acac)_6]$ (3.02 g) was dissolved in boiling benzene (20 cm^3) and piperidine (1 cm^3) added with stirring. Turquoise-blue $[Ni_2(pip)_2(acac)_4]$, which separated when the mixture was cooled to room temperature, was filtered off, washed with cold benzene, and sublimed at 100 °C and 10^{-4} mmHg, but decomposed on prolonged heating, yield 2.7 g (67%) (Found: C, 53.0; H, 7.3; N, 4.0; Ni, 17.0. Calc. for $C_{15}H_{25}NNiO_4$: C, 52.7; H, 7.3; N, 4.1; Ni, 17.2%).

*Dianilinetetrakis(pentane-*2,4-*dionato)dinickel*(II). The complex $[Ni_2(NPhH_2)_2(acac)_4]$ was prepared by the same method as the previous complex from $[Ni_3(acac)_6]$ (2.76 g) and aniline (1 cm^3), yield 2.6 g (65%) (Found: C, 54.4; H, 5.9; N, 3.9; Ni, 16.6. Calc. for $C_{16}H_{22}NNiO_4$: C, 54.9; H, 6.0; N, 4.0; Ni, 16.8%).

*Octakis(pentane-*2,4-*dionato)tetracobalt*(II). Diaquabis(pentane-2,4-dionato)cobalt(II) [14] was sublimed at 100 °C and 10^{-4} mmHg to yield purple $[Co_4(acac)_8]$. The complex was stored *in vacuo* if not used immediately after preparation.

*Tetrakis(pentane-*2,4-*dionato)(pyridine)dicobalt*(II). The complex $[Co_2(py)(acac)_4]$ was prepared in the same way as its nickel analogue, using $[Co_4(acac)_8]$ (3.25 g) and pyridine (0.5 g) in an atmosphere of dry nitrogen, yield 2.7 g (69%), m.p. 170—173 °C (Found: C, 50.3; H, 5.6; Co, 18.7; N, 2.4. Calc. for $C_{25}H_{33}Co_2NO_8$: C, 50.6; H, 5.6; Co, 18.5; N, 2.4%).

(3-*Methylpyridine)tetrakis(pentane-*2,4-*dionato)dicobalt*(II). The complex $[Co_2(3Me\text{-}py)(acac)_4]$ was prepared in the same way as $[Co_2(py)(acac)_4]$ using $[Co_4(acac)_8]$ (2.76 g) and 3-methylpyridine (0.5 cm^3). The complex was found to decompose over 2—3 weeks by losing 3Me-py, of which it smelt strongly, yield 2.1 g (63%) (Found: C, 50.8; H, 5.9; Co, 19.0; N, 2.2. Calc. for $C_{26}H_{35}Co_2NO_8$: C, 51.4; H, 5.9; Co, 19.3; N, 2.3%).

*Bis(cyclohexylamine)tetrakis(pentane-*2,4-*dionato)dicobalt*(II). The complex $[Co_2(cy)_2(acac)_4]$ could be prepared by either of the published methods [13] and purified by sublimation at 80 °C and 10^{-4} mmHg, but a purer sample of the deep red complex was given by addition of cyclohexylamine (1 cm^3) to a boiling solution of $[Co_4(acac)_8]$ (2.6 g) in benzene, yield 1.8 g (50%) (Found: C, 53.3; H, 7.5; Co, 16.5; N, 4.0. Calc. for $C_{16}H_{27}CoNO_4$: C, 53.9; H, 7.6; Co, 16.5; N, 3.9%).

*Tetrakis(pentane-*2,4-*dionato)dipiperidinedicobalt*(II). The complex $[Co_2(pip)_2(acac)_4]$ was prepared in the same way as its nickel analogue using $[Co_4(acac)_8]$ (3.02 g) and piperidine (1 cm^3) and purifying the complex by sublimation at 80 °C and 10^{-4} mmHg, although prolonged heating resulted in the formation of a purple solid, probably $[Co_4(acac)_8]$, yield 2.4 g (63%) (Found: C, 52.0; H, 7.2; Co, 16.9; N, 3.9. Calc. for $C_{15}H_{25}CoNO_4$: C, 52.7; H, 7.3; Co, 17.2; N, 4.1%).

*Dianilinetetrakis(pentane-*2,4-*dionato)dicobalt*(II). The complex $[Co_2(NPhH_2)_2(acac)_4]$ was prepared in the same way as its nickel analogue from $[Co_4(acac)_8]$ (1.38 g) and aniline (0.5 g), yield 1.1 g (60%) (Found: C, 54.5; H, 6.1; Co, 16.4; N, 3.9. Calc. for $C_{16}H_{22}CoNO_4$: C, 54.9; H, 6.0; Co, 16.8; N, 4.0%).

*Diaquabis(pentane-*2,4-*dionato)manganese*(II). The complex $[Mn(OH_2)_2(acac)_2]$ was prepared by a method adapted from that of Charles,[15] but it was necessary to exclude oxygen and light from the reaction vessels. Acetylacetone (50 g) in methanol (100 cm^3) was added to a stirred solution of $[Mn(OH_2)_4Cl_2]$ (49.5 g) in water (250 cm^3). Sodium acetate trihydrate (68.1 g) in water (150 cm^3) was added, followed by concentrated aqueous ammonia (21 cm^3). The yellow precipitate was filtered off, dried *in vacuo* over SiO_2 gel, redissolved in 95% ethanol (100 cm^3), and the solution filtered immediately. Water (15 cm^3) was added and the solution reduced to half-volume. The product was filtered off and dried *in vacuo* over SiO_2 gel. Once dry the complex is stable to air and light for 4—6 weeks before decomposing (Found: C, 40.9; H, 6.2; Mn, 18.9. Calc. for $C_{10}H_{18}MnO_6$: C, 41.5; H, 6.3; Mn, 19.0%).

(NN-*Dimethylformamide)tetrakis(pentane-*2,4-*dionato)dimanganese*(II). The original method [10] was used, yield 48% (Found: C, 47.3; H, 6.0; Mn, 19.0; N, 2.4. Calc. for $C_{23}H_{35}Mn_2NO_9$: C, 47.7; H, 6.1; Mn, 19.0; N, 2.4%).

*Bis(allylamine)tetrakis(pentane-*2,4-*dionato)dimanganese*(II). The original method [8] was used, yield 61%, m.p. 147—151 °C (Found: C, 50.2; H, 6.1; N, 4.5. Calc. for $C_{13}H_{19}MnNO_4$: C, 50.7; H, 6.2; N, 4.6%).

Analyses.—Carbon, hydrogen, and nitrogen were determined by standard microanalysis at University College, London. Metals were determined by atomic absorption spectrophotometry by Mr. S. J. Adams (Geology Department, Queen Mary College).

Magnetochemistry Measurements.—Magnetic susceptibility measurements were obtained by the Faraday technique using helium and nitrogen as cryogenic liquids in an assembly designed in this department,[16] but generally similar to that described by Cruse and Gerloch.[17] The apparatus consisted of a Sartorius 4433 vacuum microbalance with 7005

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa; 1 B.M. = 9.274×10^{-24} A m^2.

digital read-out accessory, Oxford Instrument CF200 continuous-flow cryostat, VC30 flow-control unit, DTC2 temperature controller and adaptor for sample loading, and a Newport Instruments 10-cm electromagnet with type G power supply. Samples were contained in a Teflon capsule fitted with a snap lid. The capsule could be loaded and closed in a glove-box when an air-sensitive compound was studied. A pinhole was bored through the lid to allow evacuation of the capsule and a cotton thread was used to attach the lid to the balance suspension.

Measurements were made in 1 atm helium, previously purified by passage through Na[OH] pellets and 5A molecular sieves cooled in liquid nitrogen. Values of susceptibility were obtained at three different field strengths, the balance was calibrated[18] with Hg[Co(NCS)$_4$], and the temperature was calibrated[19] with $[NH_4]_2[Mn(SO_4)_2]\cdot 6H_2O$. At least two sets of data were obtained for independently prepared samples of each compound.

RESULTS AND DISCUSSION

We have prepared the following new compounds: [Ni$_2$(4Me-py)(acac)$_4$], [Ni$_2$(3Me-py)(acac)$_4$], [Ni$_2$(cy)$_2$(acac)$_4$], [Ni$_2$(pip)$_2$(acac)$_4$], [Ni$_2$(NPhH$_2$)$_2$(acac)$_4$], [Co$_2$(3Me-py)(acac)$_4$], [Co$_2$(pip)$_2$(acac)$_4$], and [Co$_2$(NPhH$_2$)$_2$(acac)$_4$]. The complex [Ni$_2$(4Me-py)(acac)$_4$] has been proposed[20] from solution studies but not previously obtained as a solid.

Our successful preparation of crystalline [Co$_2$(py)(acac)$_4$] refutes the suggestion[21] that the first report of this was confused by a mixture of [Co$_4$(acac)$_8$] and [Co(py)$_2$(acac)$_2$]. However, solutions of the complex do disproportionate in this fashion if allowed to stand, which may account for the discrepancy.

The complexes are usually prepared by addition of a stoicheiometric quantity of base to a solution of the metal acetylacetonate in benzene. Replacement of benzene by a less hazardous solvent gives only monomeric [ML$_2$(acac)$_2$] complexes. We have also studied the reactions of 2-methylpyridine and quinoline with [Ni$_3$(acac)$_6$] but obtained only intractable solids. Attempts to prepare complexes of metal benzoylacetonates gave only amorphous solids which were hard to purify and generated such static electricity that they were a trial to handle.

The magnetic susceptibilities and moments of compounds studied over a range of temperatures are given in the Table. The results for [Co$_2$(py)(acac)$_4$] varied by 7—10% between samples but the general trend was the same. A representative set of data is given. We have also determined values of magnetic moments at room temperature for [Ni$_2$(3Me-py)(acac)$_4$] (3.28 B.M.), [Ni$_2$(4Me-py)(acac)$_4$] (3.31 B.M.), [Ni$_2$(cy)$_2$(acac)$_4$] (3.21 B.M.), [Ni$_2$(NPhH$_2$)$_2$(acac)$_4$] (3.26 B.M.), [Co$_2$(pip)$_2$(acac)$_4$] (4.94 B.M.), and [Co$_2$(NPhH$_2$)$_2$(acac)$_4$] (4.82 B.M.). The results for the aniline complexes may be less reliable than the others as the compounds decompose slightly with time.

Nickel Complexes.—The data in the Table show that both [Ni$_2$(py)(acac)$_4$] and [Ni$_2$(pip)$_2$(acac)$_4$] exhibit magnetic exchange, being respectively ferromagnetic and antiferromagnetic. The data are plotted in Figures 1 and 2. The least-squares best fit for the susceptibility of [Ni$_2$(py)(acac)$_4$] according to the HDVV model[5] gave a value of +6.0 cm^{-1} for the exchange parameter J

Magnetic susceptibilities (c.g.s. units) and moments (B.M.)

[Ni$_2$(py)(acac)$_4$]		
T/K	$10^3\chi_{Ni}$	$\mu_{eff.}$
298	4.56	3.30
273	5.00	3.29
223	6.03	3.28
173	7.57	3.24
123	10.69	3.24
98	13.31	3.23
80	16.12	3.21
73	18.00	3.24
63	20.8	3.24
53	25.8	3.31
42	35.6	3.46
36	39.5	3.37
28	54.1	3.48
25	66.9	3.66
23	69.8	3.58
19	87.5	3.65
15	110.0	3.63
14	117.8	3.63
11	186.5	4.05
7	266.6	3.86
4	448.2	3.79

[Ni$_2$(pip)$_2$(acac)$_4$]		
T/K	$10^3\chi_{Ni}$	$\mu_{eff.}$
300	3.90	3.06
275	4.24	3.05
225	5.10	3.03
175	6.36	2.98
125	8.60	2.93
100	10.56	2.91
80	13.34	2.92
70	14.49	2.85
60	16.33	2.80
54	17.81	2.77
45	20.3	2.70
41	21.5	2.66
36	23.1	2.58
30	24.0	2.40
26	25.2	2.29
23	26.3	2.20
20	26.5	2.06
18	26.9	1.97
15	25.8	1.76
14	24.4	1.65
12	24.0	1.52
11	22.5	1.41
7	19.69	1.05
4	10.89	0.59

[Co$_2$(py)(acac)$_4$]		
T/K	$10^3\chi_{Co}$	$\mu_{eff.}$
300	10.80	5.09
263	11.83	4.99
163	19.15	5.00
115	26.8	4.97
93	32.7	4.93
90	34.1	4.96
76	36.9	4.74
69	40.7	4.74
59	45.3	4.62
51	55.3	4.75
40	68.8	4.69
28	80.5	4.25
25	85.9	4.14
21	95.1	4.00
17	112.6	3.91
12	139.6	3.66
9	182.3	3.62
4	421.4	3.43

[Co$_2$(cy)$_2$(acac)$_4$]		
T/K	$10^3\chi_{Co}$	$\mu_{eff.}$
300	10.50	5.02
275	11.36	5.00
223	13.06	4.83
173	16.53	4.78
123	21.1	4.56
80	27.8	4.22
72	30.1	4.16
63	32.9	4.07
53	41.2	4.18
43	45.5	3.96
29	62.1	3.80
25	70.2	3.75
20	85.0	3.69
14	102.2	3.38
10	121.1	3.11
7	147.3	2.87
4	127.8	2.02

[Mn$_2$(dmf)(acac)$_4$]		
T/K	$10^3\chi_{Mn}$	$\mu_{eff.}$
300	14.06	5.81
263	15.74	5.75
212	19.37	5.73
163	24.9	5.70
115	33.9	5.58
93	41.5	5.56
90	43.7	5.61
80	45.3	5.38
73	49.0	5.35
70	49.4	5.26
60	54.4	5.11
52	63.6	5.14
40	77.0	4.96
30	91.5	4.69
25	100.2	4.48
21	109.1	4.28
17	120.3	4.04
14	131.9	3.84
11	143.3	3.55
7	155.1	2.95
4	174.0	2.36

[Mn$_2$(all)$_2$(acac)$_4$]		
T/K	$10^3\chi_{Mn}$	$\mu_{eff.}$
300	16.05	6.21
290	16.60	6.21
263	18.25	6.20
212	22.7	6.20
163	29.2	6.17
115	40.0	6.07
93	48.0	5.98
90	49.3	5.96
76	53.2	5.69
73	57.3	5.78
59	64.9	5.53
51	72.5	5.44
40	82.8	5.15
29	95.2	4.70
25	103.1	4.54
21	112.3	4.34
17	127.2	4.16
12	169.8	4.04
9	229.2	4.06
4	499.6	4.00

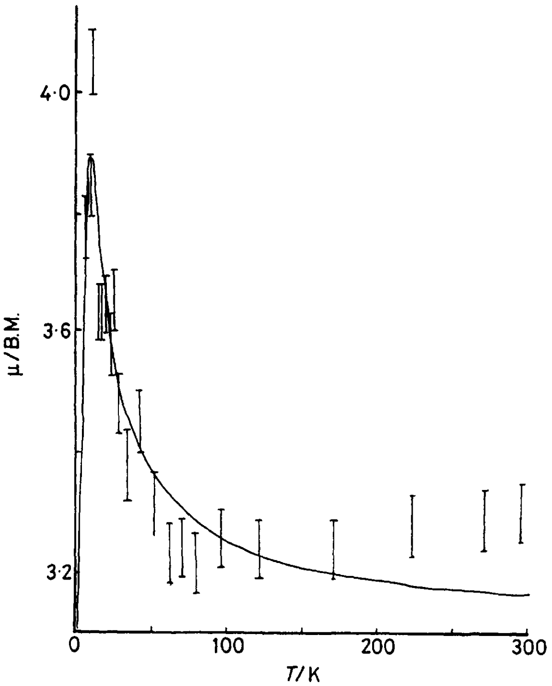

FIGURE 1 Temperature dependence of the magnetic moment of $[Ni_2(py)(acac)_4]$. Curve shows values for $J = +4.3$ cm^{-1}, $g = 2.20$, $D = -11.4$ cm^{-1}, and $ZJ' = +0.29$ cm^{-1}

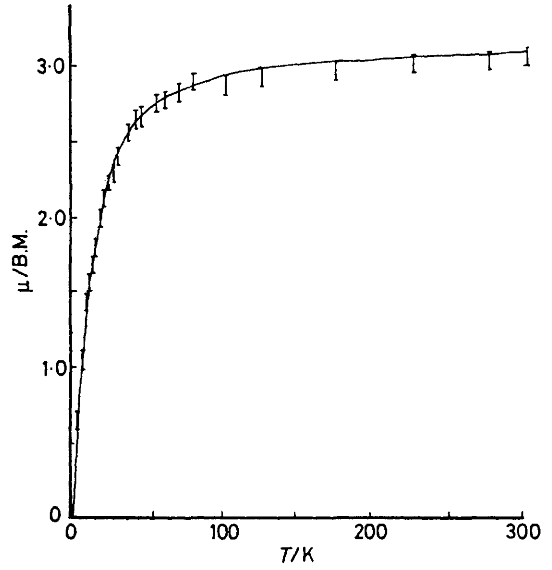

FIGURE 2 Temperature dependence of the magnetic moment of $[Ni_2(pip)_2(acac)_4]$. Curve shows values for $J = -6.1$ cm^{-1}, $g = 2.24$, $D = -13.7$ cm^{-1}, and $ZJ' = -0.41$ cm^{-1}

and 2.20 for g. A better fit was given by including zero-field splitting and intermolecular exchange in the modified equation devised by Ginsberg *et al.*,[22] giving $J = +4.3$ cm^{-1}, $g = 2.20$, $D = -11.4$ cm^{-1}, and $ZJ' - +0.29$ cm^{-1}. For $[Ni_2(pip)_2(acac)_4]$ the HDVV model gives $J = -5.9$ cm^{-1} and $g = 2.15$, and the Ginsberg equation again gives a better fit, with $J = -6.1$ cm^{-1}, $g = 2.24$, $D = -13.7$ cm^{-1}, and $ZJ' = -0.41$ cm^{-1}. These values are comparable with those for other nickel(II) dimers derived from magnetochemical measurements, *e.g.* $J = +4.5$ cm^{-1}, $g = 2.14$, $D = -3.3$ cm^{-1}, and $ZJ' = -1.5$ cm^{-1} for $[Ni_2(en)_4(SCN)_2]I_2$ (en = ethylenediamine) (ref. 22); $J = -15.7$ cm^{-1}, $g = 2.198$, $D = +13.7$ cm^{-1}, and $ZJ' = 0.20$ cm^{-1} for $[Ni_2(trien)_2(C_2O_4)][ClO_4]_2$ (trien = triethylenetetra-amine) (ref. 23).

The striking difference in the magnetic properties of the two nickel complexes can be explained by their different structures,[7] which give NiONi bridging angles of 86.7—88.5° for $[Ni_2(py)(acac)_4]$ and 99.6° for $[Ni_2(pip)_2(acac)_4]$. The former values are similar to the bridging angles of 83.1—87.4° found in $[Ni_3(acac)_6]$, which also has a face-shared octahedral structure and is also ferromagnetic.[5,24] Clearly the exchange processes in $[Ni_3(acac)_6]$ and $[Ni_2(py)(acac)_4]$ are similar. However, the wider NiONi bridging angle in the piperidine complex must allow some significant overlap of two nickel e_g orbitals with the same $2p$ orbital on the bridging oxygen, giving rise to antiferromagnetism. The change from ferromagnetism to antiferromagnetism as the bridging angle increases is similar to that discovered in binuclear copper(II) hydroxy-complexes.[6]

Recent papers have warned against reliance on the magnitude of the bridging angle as a sole guide to magnetic properties and have stressed the possible importance of such factors as differing stereochemistry at the metal atoms [25] and the role of non-bridging ligands.[26] Separating the contributions from these various factors is bound to be difficult. The detection of ferromagnetism in $[\{Ni(OMe)(acac)(HOMe)\}_4]$ (ref. 27) (NiONi bridging angle 94.6—98.6°) and in $[\{Ni(OMe)(OC_6H_4CHO)(HOEt)\}_4]$ (ref. 28) (bridging angle *ca.* 98°) shows this is a subtle problem in nickel(II) clusters as well as copper ones. The effect of subtleties in the stereochemistry at the nickel atom may apply here, because both the ferromagnetic complexes are trigonally elongated along the Ni–Ni axis with O(bridge)–Ni–O(bridge) angles down to 73.1° for $[Ni_3(acac)_6]$ and 74.9° for $[Ni_2(py)(acac)_4]$, whereas the antiferromagnetic $[Ni_2(pip)_2(acac)_4]$ is much closer to a regular octahedron round the nickel atoms. We have prepared a number of pyrazole and imidazole complexes of nickel(II) acetylacetonate to give clearer insight into this problem.[29]

Cobalt Complexes.—The magnetic properties of the cobalt(II) complexes contrast remarkably with those for the nickel analogues. For both $[Co_2(py)(acac)_4]$ and $[Co_2(cy)_2(acac)_4]$ the magnetic susceptibility and the magnetic moment each decrease with temperature. However, this does not necessarily imply antiferromagnetism since even monomeric octahedral cobalt(II) complexes show such a decrease because of the extensive spin–orbit coupling shown in the $^4T_{1g}$ ground state. It is possible that the less marked decrease in moment shown by $[Co_2(py)(acac)_4]$ is due to weak ferromagnetism opposing the reduction in spin–orbit coupling, but it is not reasonable to calculate such an effect because it must be very small and, as recorded above, we found it hard to obtain reproducible data for this complex. The presence of one unpaired electron in a t_{2g} orbital on each cobalt atom may in principle generate ferromagnetism, provided the t_{2g} orbitals are not extensively involved in π bonding. Such an effect may occur in either dimeric structure but should be greater in $[Co_2(py)(acac)_4]$, where the two cobalt atoms are closer.

The explanation for the difference in magnetic interaction between the nickel and cobalt pyridine complexes may lie in their different metal–oxygen bond lengths in the bridging units.[7] The Ni–O(bridge) bond length averages 2.083 Å but the Co–O(bridge) bond length averages 2.130 Å; the shortest Ni–O–Ni superexchange path is 4.139 Å, the shortest Co–O–Co path is 4.235 Å. Thus metal–ligand overlaps and magnetic interactions are greater for the nickel dimer than the cobalt dimer. For the edge-shared dimers the Ni–O(bridge) bond is 2.156 Å, but is not significantly shorter than the average Co–O(bridge) bond of 2.164 Å in $[Co_2(cy)_2(acac)_4]$. Therefore no appreciable difference is expected between the antiferromagnetism of $[Ni_2(pip)_2(acac)_4]$ and $[Co_2(cy)_2(acac)_4]$, and this is confirmed by the data, which show the former compound to be only weakly antiferromagnetic and the effects of exchange in the latter to be masked by the spin–orbit coupling. In short, we consider that our cobalt complexes show no significant differences in magnetism from mononuclear six-co-ordinate cobalt(II) complexes.

Manganese Complexes.—The magnetic moments of both our manganese complexes decrease with temperature, but the data correspond to J values of only about -1 cm^{-1}, which represents only very weak antiferromagnetism, also shown by low Weiss constants of 20 K. The high-temperature moment for $[Mn_2(all)_2(acac)_4]$ is higher than the spin-only value of 5.92 B.M., and this discrepancy probably indicates the presence of some paramagnetic impurity, although data from different samples were identical within experimental error. We found manganese(II) acetylacetonate was easily oxidized in solution, and this oxidation is hastened in the light, so some low-molecular-weight manganese(III) species may be present.

Conclusion.—There is a serious shortage of binuclear complexes which can be prepared with a full range of first-row transition metals and give a comparative study of structure and magnetism. Michalowicz *et al.*[30] studied some oxalate complexes of bivalent metals from iron to copper and found, as we have for diketonates, that magnetic interactions are greater with increased atomic number, but there were some structural differences along their series. A similar trend occurs in compounds of the type $[M_2L_2(OH)_2][ClO_4]_2$ (M = Ni or Cu; L = macrocyclic triamine), where the nickel complex is less antiferromagnetic than the copper complex, whose antiferromagnetism was evident at room temperature, but the cobalt(II) complex was not stable.[31] However, such oxalate-bridged dimers as $[M_2(dien)_2(C_2O_4)][ClO_4]_2$ (dien = diethylenetriamine) show a reverse trend with the copper complex magnetically normal and the nickel complex antiferromagnetic; the anomaly was attributed[32] to differing overlap of the oxalate orbitals with the metal d_{z^2} and $d_{x^2-y^2}$ orbitals. The acetylacetonate complexes reported here and others still under investigation[29] should give a more extensive series, although we do not expect to prepare copper(II) dimers, since $[CuL(acac)_2]$ complexes are five-co-ordinate monomers in crystalline[33] and solution[34] states.

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