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Magnetic Properties of Polynuclear Complexes. Part I. Superexchange in Some Binuclear Nickel(II) Complexes

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The magnetic susceptibilities of a number of binuclear nickel(II) complexes between 80 and 300°K are reported. Most of the compounds exhibit antiferromagnetic exchange, and a curve-fitting procedure is used to obtain values of the exchange parameter J. The compounds studied include Ni₂ paa₃X₄,nH₂O (paa = pyridine-2-aldazine; X = I, ClO₄, or BF₄), Ni₂ dppn₂X₄,nH₂O (dppn = 3,6-di(pyrid-2-yl)pyridazine; X = NO₃ or ClO₄), Ni₂ dppl(NO₃)₂, 2H₂O [dppIH = 3,5-di(pyrid-2-yl)pyrazole, a new compound], Ni₂ dphp₂X₄,nH₂O (dhph = 1,4-dihydrazinophthal-azine; X = Cl, Br, or I), and Ni₂ en₄(C₂O₄) (NO₃)₂. The values of J for these and other binuclear nickel(II) complexes are discussed in terms of superexchange mechanisms.

A RECENT compilation of magnetochemical data¹ lists some 94 binuclear complexes of copper(II), many of which have been studied in great detail. In contrast, only six supposedly binuclear nickel(II) complexes are listed, none of which have been studied magnetically over a temperature range.

Stratton and Busch reported apparently binuclear iron(II), cobalt(II), nickel(II), and copper(II) complexes of pyridine-2-aldehyde azine (paa) (I).² We have prepared and studied magnetically a number of nickel(II) and cobalt(II) complexes of 3.6-di(pyrid-2-yl)pyridazine (dppn) (III), 3,6-di-(6-methylpyrid-2-yl)pyridazine (Me₂dppn) (III), 3,5-di(pyrid-2-yl)pyrazole (dpplH) (IV), and 1,4-dihydrazinophthalazine (dhph) (V). These

complexes also appear to be binuclear, with each atom of the N-N group co-ordinated to one of the two metal



² W. J. Stratton and D. H. Busch, J. Amer. Chem. Soc., 1956, 78, 1137; 1958, 80, 1286; 1960, 82, 4833.

¹ Landolt-Bornstein, New Series, Group II, Volume 2, [']Magnetic Properties of Coordination and Organo-metallic Transition Metal Compounds,' by E. König, Springer-Verlag, Berlin, 1966.

There are two interesting questions about this series of complexes: (a) how does the strength of the spin-spin interaction depend upon the nature of the metal ions

twisted by some 60° about its N-N bond. The magnetic properties are also in agreement with a binuclear structure.

Complexes of (II) and (III). The electronic spectra of the grey-green nickel complexes $Ni dppn(NO_3)_2, H_2O$

The comp	ounds studied a	nd their magn	etic parameter	s			
Compound	Colour	$\mu_{ m eff}~(300^{\circ}{ m \kappa})$	$\mu_{ m eff}~(100^\circ{ m \kappa})$	$-\theta$	g	-J/k	$10^2 R$
Ni, paa, I, 4H, O	Red	2.97	2.75	27°	2.16	13·7°	0.84
Ni_{a} paa ₃ (ClO_{a}) ₄ , 2H ₂ O	Yellow	2.95	$2 \cdot 80$	19	$2 \cdot 12$	8.3	0.62
$Ni_2 paa_3(BF_4)_4, 2H_2O$	Yellow	2.96	2.79	21	2.13	$9 \cdot 9$	0.72
Ni dppn $(NO_3)_2$, H_2O^a	Grey-green	2.91	2.37	89	$2 \cdot 21$	33.8	0.58
Ni dppn(ClO_4) ₂ , $2H_2O$	Grey-green	2.91	2.55	54	2.15	$21 \cdot 1$	1.09
$Ni_2 dppn(SO_4)_2, 5H_2O$	Green	2.87	2.67	34	2.18	17.7	0.07
$Ni_{2}(Me_{2}dppn)(NO_{3})_{4}, 2H_{2}O$	Green	2.89	2.36	84	2.18	29.8	1.05
$Ni_2(Me_2dppn)(NO_3)_4, H_2O, CH_3OH$	Green	2.91	2.43	76	2.18	26.6	0.87
$Ni(Me_2dppn)_2(ClO_4)_2, 2H_2O$	Pale green	3.09	2.99	6	$2 \cdot 20$		
Ni dppl NO ₃ , H ₂ O	Lavender	2.92	2.54	56	$2 \cdot 20$	$25 \cdot 1$	0.85
Ni dppl NO ₃ , ¹ / ₂ H ₂ O, ¹ / ₂ CH ₃ OH	Lavender	2.92	2.58	50	2.18	$22 \cdot 4$	0.66
Ni dhph Cl ₂ ,3H ₂ O	Purple	2.82	2.30	93	$2 \cdot 15$	$32 \cdot 1$	0.54
Ni dhph Br ₂ ,3H ₂ O ^a	Purple-grey	2.79	2.28	90	2.16	34.3	0.78
Ni dhph I. 3H.O	Grey	2.81	2.33	77	2.14	30.7	1.17
Ni dhph Cl ₂ ,2H ₂ O	Grey	2.80	$2 \cdot 24$	103	2.14	33.8	0.69
Ni dhph Br, 2H, O	Grey	2.84	2.27	85	2.19	35.3	0.06
Ni dhph $Cl_{2,\frac{1}{2}}H_{2O}$	Green	2.87	2.30	86	2.19	34.0	0.82
Ni dhph Br, H,O	Yellow-brown	2.89	$2 \cdot 31$	92	$2 \cdot 21$	33.9	0.51
Ni dhph I_2, H_2O	Yellow-brown	2.84	2.27	95	2.18	34.6	0.72
$Ni_{a} en_{a} ox(NO_{a})$,	Blue-violet	2.94	2.56	52	2.19	23.0	1.19
Ni_{2} dien ₂ $ox(NO_{3})_{2}$, $H_{2}O$	Blue	2.92	2.58	47	2.16	21.0	0.91
Ni ₂ trien ₃ Cl ₄ , 2H ₂ O	Violet	2.94	2.83	12	2.11	8.0	1.15

TABLE 1

^a Magnetic parameters are weighted averages of results for two different samples of this compound.

(and in particular on the relative occupancy of the e_g and t_{2g} orbitals); and (b) how does it depend on the structure of the bridging system? In another paper we have sought an answer to the first question from a comparison of some of the cobalt and nickel complexes.³ We here examine the binuclear nickel complexes of the ligands (I)—(V), and of certain other nickel complexes that are thought to be binuclear, in the hope of answering the second question.

The compounds are listed in Table 1. They are all paramagnetic, with $\mu_{\text{eff}} = ca. 2.8 - 2.9$ B.M. at room temperature, indicating sixfold co-ordination of Ni²⁺. We begin by presenting the evidence for their formulation as binuclear.

Structures of the Complexes.—Complexes of (I). Stratton and Busch² present convincing evidence for formulating the compounds $M_2 paa_3 X_4, nH_2O$ (M = Fe or Ni; X = I, ClO₄, or BF₄; n = I or 2) as salts containing binuclear $[M_2 \text{ paa}_3]^{4+}$ cations, on the basis of (a) their molar conductance in aqueous solution; (b) the diamagnetism of the iron(II) complexes; and (c) a study of the infrared spectra, which do not show the splitting of a pyridine band and the doubling of the C=N stretching frequency characterised as typical of pyridinaldazine in terdentate co-ordination. The last observation rules out a structure involving one bridging and two terdentate paa molecules, leaving (VI) as the only reasonable structure. Experiments with models indicate that this is quite feasible sterically, provided that each ligand is ³ J. E. Andrew, P. W. Ball, and A. B. Blake, Chem. Comm., 1969, 143.

(Figure, curve 2) and Ni dppn(ClO_4)₂, $2H_2O$ show four bands at about 10,000, 12,000, 17,000, and 18,000 cm.⁻¹, with intense absorption above 22,000 cm.⁻¹. By



Electronic spectra of solid complexes. The assignments at the top of the diagram refer to local symmetry D_{4h} , those at the bottom to O_h . Curve 1, Ni dhph Cl₂,3H₂O; 2, Ni dppn(NO₃)₂,-H₂O; 3, Ni(Me₂dppn)₂(ClO₄)₂,2H₂O; 4, Ni₂(Me₂dppn)(NO₃)₄,-2H₂O

assuming a tetragonal crystal field, a satisfactory interpretation of the spectra is possible; the suggested assignments are shown in Table 2, together with values of the mean Dq and Racah B parameters calculated in the octahedral approximation.⁴ In contrast, the spectra of the green complexes Ni₂ dppn(SO₄)₂,5H₂O and Ni₂(Me₂dppn)(NO₃)₄,2H₂O (curve 4) contain only two broad bands below 22,000 cm.⁻¹, at about 10,000 and 16,500 cm.⁻¹. These clearly correspond to the first two transitions of an approximately octahedral nickel complex. The spectrum of the presumably mononuclear (VIII) is suggested for the compounds with a 2:1 metal: ligand ratio. As will be shown below, these binuclear structures are also in agreement with the magnetic properties of the compounds.

It may be objected that a structure such as (VII) would be unstable for the same reason that bis-(2,2'-bipyridyl) complexes of cobalt(II) and nickel(II) exist only in the *cis*-form, *i.e.*, (presumably), steric interference between the 6-hydrogen atoms of the pyridine rings. Experiments with molecular models (Prentice-Hall) indicate that in the dppn complexes this interference can

	Electronic (re	eflectance)	spectra				
Absorption maxima (cm1) and assignments							
Compound $O_{4k}: {}^{3}A_{2g} \rightarrow D_{4k}: {}^{3}B_{1g} \rightarrow$	$\rightarrow {}^{3}E_{g}$	³ B _{2g}	${}^{3}A_{2g}$	${}^{3}T_{1g}(F)$	³ Е _g	Dq	В
Ni dppn $(NO_3)_2, H_2O$),200),400	12,000sh 11,900sh	16,600sh 16,950sh		$18,450 \\ 17,850$	$\begin{array}{c} 1080 \\ 1125 \end{array}$	1080 1010
Ni ₂ dppn(SO ₄),5H ₂ O Ni ₂ (Me ₂ dppn)(NO ₃) ₄ ,2H ₂ O	10,200 10,000	·	·	$16,750 \\ 16,400$,	$\begin{array}{c} 1020 \\ 1000 \end{array}$	1020 990
$Ni(Me_2dppn)(Cl_2O_4)_2, 2H_2O$ Ni dppl NO_3, H_2O	10,200 8750	12,850sh	13,150	17,700	18,150	$\begin{array}{c} 1020 \\ 1010 \end{array}$	$1085 \\ 925$
Ni dppl NO ₃ ,0·5H ₂ O,0·5CH ₃ OH Ni dhph Cl ₂ ,3H ₂ O	8700 9600	12,550sh 13,200sh	13,200 13,800		$17,850 \\ 18,900$	$\begin{array}{c} 1000 \\ 1080 \end{array}$	925 1030
Ni dhph Br, 3H,0 Ni dhph I, 3H,0	9350 9550	13,900 13,200sh	14,250sh ª 13,900		$19,000 \\ 19,000$	$\begin{array}{c} 1085 \\ 1075 \end{array}$	$1045 \\ 1040$
Ni dhph $\tilde{Cl}_{2,0}$. \tilde{sH}_{2O} Ni dhph $Br_{2,1}H_{2O}$	8600 8350	14,400 13,800		$16,500 \\ b$		$\begin{array}{c} 1055\\ 1015 \end{array}$	985
Ni dhph I ₂ ,H ₂ O sh, shoulder. ^a Observed only in a	8300 a mull spectrum at	13,900 77°к. ^в С	bscured by	b intense cha	.rge-transfe	1015 absorption	

TABLE 2

complex $Ni(Me_2dppn)_2(ClO_4)_2, 2H_2O$ (curve 3) is very similar. The much greater splitting of the octahedral energy levels in the complexes with a 1:1 metal: ligand



ratio, compared with those with a 2:1 or a 1:2 ratio, strongly suggests that the arrangement of ligand atoms in the former type is $trans-N_4O_2$ (in the latter types it is presumably $cis-N_2O_4$ and $cis-N_4O_2$ respectively), and the simplest structure consistent with this co-ordination is the binuclear arrangement (VII). A structure such as

⁴ See, e.g., B. N. Figgis, 'Introduction to Ligand Fields,' John Wiley, New York, 1966. be accommodated: there is only one such $H \cdots H$ contact per four metal-ligand bonds, instead of two as in the bipy complexes, and the dppn molecule has to distort only half as much as the bipy molecule in order to relieve the pressure. Steric interference in 1:1 complexes of Me₂dppn would be much more severe, of course, and only 1:2 and 2:1 complexes were in fact obtained with this ligand.

The i.r. spectra of the nitrates (Table 3) indicate that the anions are co-ordinated.⁵ The strong band at about 1030 cm.⁻¹ is probably the v_1 band of NO₃⁻ (corresponding to the totally symmetric N-O stretch) rendered i.r.active by co-ordination, and the splitting of v_3 into the strong bands at *ca*. 1300 and *ca*. 1450 cm.⁻¹ is also consistent with co-ordination of NO₃⁻. In the 1:1 complexes the co-ordination is probably unidentate. In the spectra of the 2:1 complexes, the breadth of the 1300 cm.⁻¹ band and the appearance of two bands in the region of 825 cm.⁻¹, where the non-degenerate v_2 mode is expected to absorb, suggest the presence of two kinds of co-ordinated nitrate ions (possibly both uni- and bi-dentate).

In the sulphate, the presence of bands at 480 and 960 cm.⁻¹ and of at least three strong bands in the 1100 cm.⁻¹ region suggests bidentate co-ordination of the anions.⁶ The i.r. spectra of the perchlorates show no definite evidence for co-ordination of the anions.

 ⁵ N. F. Curtis and Y. V. Curtis, *Inorg. Chem.*, 1965, 4, 805.
 ⁶ K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, 79, 4904.

Complexes of (IV). Again, the evidence for a binuclear formulation is indirect. From the stoicheiometry it is evident that the ligand is present as its anion, and this is confirmed by the i.r. spectrum. The N-H stretching vibration of the pure ligand in chloroform solution gives a sharp, medium-intensity band at 3445 cm.⁻¹, while in the solid (KCl disc or hexachloro-

The only reasonable structure consistent with all of the above observations is the binuclear arrangement (IX), analogous to the structure deduced for the dppn complexes (VII), and that demonstrated (see below) for the dhph complexes (X).

Complexes of V. The crystal structure of Ni dhph $Cl_2, 3H_2O$ has recently been determined by X-ray

TABLE 3 I.r. spectra: bands assigned to anion vibrations Absorption maxima (cm⁻¹) and assign

		Absor	stion maxima (cm	· ·) and assignm	ents "	
Compound NO ₃ -	-: v ₃ (E′)	$\nu_1 b (A_1')$	ν2(Α	2 ^{''})	$\nu_4(E')$
Ni dppn $(NO_3)_2, H_2O$	1445s, br	1300s,br	1023s	814	ms	737w
$Ni_{2}(Me_{2}dppn)(NO_{3})_{4}, 2H_{2}O$ Ni dppl $NO_{3}, H_{2}O$	$1460 \mathrm{s,vb}$ $1420 \mathrm{s,vb}$	1320s,vb 1315s,br	1040m 1030s	828m	815w	720w
SO4 ²	$\nu_{3}($	T ₂)	$\nu_1 b (A_1)$	$\nu_4(7)$	_ 2)	$\nu_2 b (E)$
$Ni_2 dppn(SO_4)_2, 5H_2O$	1190s 1093s	1144s 1077s	958m,br	625s,br	610s,br	480ms,br

^a Symmetry species of unco-ordinated anion are given in parentheses. Mode inactive in unco-ordinated anion. s, strong; m, medium; w, weak; br, broad; vb, very broad.

butadiene mull) it appears as a strong, broad band at 3210 cm.^{-1} , shifted to 2395 cm.^{-1} after refluxing in D₂O (it is probable that the compound exists as hydrogenbonded dimers in the crystal). The spectra of the nickel complexes show only a very broad band between 3100 and 3600 cm.⁻¹, and a sharp, medium band at 3630 cm.⁻¹, both of which are probably due to vibrations of coordinated water. Since under the conditions used it is unlikely that displacement of the imino-proton would occur before co-ordination of the other pyrazole N atom, and then only if accompanied by chelation (*cf.* phthalocyanine), we infer that all four of the ligand N atoms are co-ordinated. A similar conclusion is reached from a consideration of the number of available donor atoms per nickel ion.

The electronic spectra of the two complexes (Table 2) can be interpreted by assuming a substantial tetragonal distortion of the crystal field, such that the bands at ca. 8700 and ca. 12,700 cm.⁻¹ correspond to the two components into which the ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ transition is split by the axial field, and those at ca. 13,200 and ca. 18,000 cm.⁻¹ to the components of the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ transition. The suggested assignments are shown in Table 2, together with values of the mean Dq and Racah B parameters. The magnitude of the axial-field splittings is similar to that in the dihydrazinophthalazine complexes (see below) and even larger than that in the dipyridylpyridazine 1:1 complexes, and, as in the latter case, is taken to indicate *trans*- rather than cis-N₄O₂ co-ordination.

To satisfy the stoicheiometry it must be assumed that the nitrate ions are co-ordinated, and this is again supported by the i.r. spectra (Table 3), the main evidence being the intensity of the band at 1030 cm.⁻¹ and the splitting of the nitrate v_3 band into two components at 1315 and *ca.* 1420 cm.⁻¹. Unfortunately the profusion of ligand bands in the 700–900 cm.⁻¹ region prevents definite identification of the nitrate v_2 and v_3 bands. methods.⁷ The cation has the centrosymmetric binuclear structure (X), with the nickel atoms in approximately octahedral co-ordination (Ni–N = 2.07-2.10 Å,



Ni–O = $2 \cdot 16$ Å) and Ni–N–N–Ni angles of about 125°. The Ni–Ni distance is $3 \cdot 79$ Å.

The electronic spectra of the purple trihydrates Ni dhph $X_{2,3}H_{2}O$ (X = Cl, Br, or I) are similar, and consist of three broad bands at approximately 9400, 13,500, and 18,800 cm.⁻¹ (Figure, curve 1). The central band is split into two components which are poorly

⁷ J. E. Andrew and A. B. Biake, preceding paper.

resolved even at low temperatures, with a splitting of ca. 700 cm.⁻¹. A satisfactory interpretation is again possible if the octahedral ${}^{3}T_{2g}$ and ${}^{3}T_{1g}(F)$ levels are assumed to be split by some 4000-5000 cm.⁻¹ by the tetragonal ligand field, so that two of the resulting four levels almost coincide.

Heating the trihydrates under vacuum gives various lower hydrates. When the number of water molecules falls below two per Ni atom the colour changes to green (Ni dhph Cl₂, 0.5H₂O) or yellow-brown (Ni dhph X₂, H₂O, X = Br or I) and the spectrum is altered by the appearance of intense absorption above 17,500 cm.⁻¹ (Cl) or ca. 15,000 cm.⁻¹ (Br or I), with a shift of the lowestenergy band some 1000 cm.⁻¹ towards the red. The magnetic properties are substantially unchanged, however, and these compounds evidently contain axially co-ordinated halide ions.

Other compounds. The nickel amine hemioxalate complexes were first prepared by Curtis,⁸ who assigned structures of the type (XI) to them on the basis of their i.r. spectra. This has recently been confirmed by an X-ray determination of the structure of $[Ni en_2 ox]$ -(NO₃)₂.⁹

TABLE 4

Magnetic susceptibilities (c.g.s. units per formula weight, after correction for t.i.p. and diamagnetism as described in the text)

<i>Т</i> (°к)	10 ⁶ χ	$T(^{\circ}\kappa)$	10 ⁶ χ	$T(^{\circ}\kappa)$	10 ⁶ χ		
Ni, paa	.I4H.O	$\operatorname{Ni}_2\operatorname{paa}_3$ 2H	$Ni_2 paa_3(ClO_4)_4, 2H_2O$		$_{3}(BF_{4})_{4},$		
206.8	7425	297.0	7325	297.2	7385		
270.0	8182	260.8	8312	269.2	8021		
240.8	8951	241.5	9017	240.0	9006		
209.5	10.064	208.2	10.126	207.2	10.111		
177.4	11.572	176.0	11.773	175.2	11.810		
148.2	13,932	148.9	13,807	147.4	14,078		
119.4	16,532	120.8	16,653	120.5	16,505		
$102 \cdot 9$	18,673	101-1	19,643	97.1	19,932		
84.8	21,332	86.8	22,429	77.1	24,172		
	·	82.4	23,367				
Ni ₂ dpp 2H	$Ni_2 dppn_2(NO_3)_4, 2H_O$		n ₂ (NO ₃) ₄ , 1 ₂ O	$Ni_2 dppn_2(ClO_4)_4, 4H_2O$			
Sam	ple 1	Sam	ple 2		2		
299.4	7072	297.0	7100	297.1	7122		
293.0	7212	253.0	8028	269.8	7805		
247.0	8126	223.0	8872	239.3	8626		
205.0	9361	171.0	10,552	210.0	9492		
173.0	10,503	150.0	11,492	187.6	10,270		
158.2	11,176	132,0	12,036	155.6	11,872		
147.0	11,637	95.0	14,334	133.8	13,298		
$115 \cdot 1$	13,187	88.0	14,654	111.6	15,110		
$102 \cdot 9$	13,914	82.0	14,828	93·4	16,849		
89.8	14,421	80.0	14,908	77.8	18,797		
84 ·2	14,733						
$Ni_2 dppn(SO_4)_2$,		$Ni_2(Me_2dp)$	$Ni_2(Me_2dppn)(NO_3)_4$,		$Ni_2(Me_2dppn)(NO_3)_4$		
$5H_2O$		2H	1 ₂ O	H ₂ O,MeOH			
298.8	7344	294.8	7070	297.0	7167		
$273 \cdot 8$	7919	271.4	7516	266.6	7764		
236.9	8997	$245 \cdot 2$	8148	242.0	8503		
$202 \cdot 0$	10,361	209·6	9149	$212 \cdot 4$	9170		
174.5	11,727	189.2	9755	185.4	10,152		
130.9	14,764	159.7	10,849	148.6	11,867		
102.8	17,607	129.9	12,285	123.0	13,414		
91.0	19,090	110.6	13,451	107.9	14,525		
83.1	20,191	95.6	14,414	89.3	15,796		
		81.3	15,251	86.2	16,132		
				77.0	16,862		

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Ni(Me ₂ dpp 2H	on) ₂ (ClO ₄) ₂ , I ₂ O	Ni ₂ dpp 2H	l ₂ (NO ₃) ₂ , l ₂ O	Ni ₂ dppl H ₂ O,N	2(NO3)2, MeOH
297.5	4015	$295 \cdot 8$	7280	299 ·8	7167
269.7	4363	271.6	7740	273.0	7797
245.7	4830	240.6	8616	$242 \cdot 2$	8685
217.4	5344	212.2	9536	211.6	9719
109.9	5000	180.7	10 752	177.2	10 975
152.2	7500	151.5	10,702	149.1	10,010
101.2	1000	101.0	14,414	149.1	12,047
123.2	9117	118.3	14,002	107.7	10,797
96.0	11,672	104.0	15,856	94.0	17,029
80.2	13,869	86.4	16,970	85.8	17,859
		78.1	17,570	78.7	18,001
Ni ₂ dhph	₂ Cl ₄ ,6H ₂ O	Ni ₂ dhph	$_{2}Br_{4}, 6H_{2}O$	Ni ₂ dhpi	1 ₂ 1 ₄ ,6H ₂ O
200 0	6600	007.9	2000	906.9	866A
298.0	0022	291.8	0000	290.2	0004
273.0	7106	202.0	7330	273.3	7000
224.5	8274	230.2	8049	239.0	7830
$204 \cdot 1$	8778	198.6	8953	210.4	8659
170.5	9953	174.7	9835	176.5	9658
1 49 ·0	10,762	134.2	11,391	146.6	11,062
126.0	11,922	108-1	12,662	113.2	12,902
104.2	13.062	95.8	13.067	98.9	13.655
87.5	13 702	87.6	13 163	92.5	13,802
82.0	13 842	79.4	13 313	79.0	14 114
79·0	13,942	10 1	10,010	100	
Ni ₂ dhph ₂ Sam	Br ₄ ,6H ₂ O	Ni_2 dhph	₂ Cl ₄ ,4H ₂ O	Ni2 dhph	₂ Br ₄ ,4H ₂ O
00 m 0	P10 2	001.0	6650	900.F	6770
297.8	0000	291.2	0002	290.0	0770
262.6	7192	271.0	7006	271.0	7293
230.2	7892	243.2	7647	235.4	8121
198.6	8780	214.2	8317	204.5	8973
174.7	9646	$183 \cdot 1$	9160	163.5	10,354
134.2	11,174	152.0	10,407	125.9	11,858
108-1	12,452	$125 \cdot 4$	11,418	98 .6	12,940
95 ·8	12,820	99.6	12,456	$82 \cdot 9$	13,390
87.0	12,914	88.1	12,958	77.0	13,483
79.4	13,062	78.2	13,282		
Ni ₂ dhph	$_{2}Cl_{4},H_{2}O$	Ni ₂ dhph	$_{2}\mathrm{Br}_{4}, 2\mathrm{H}_{2}\mathrm{O}$	Ni_2 dhpl	1 ₂ I ₄ ,2H ₂ O
290.4	7017	296.5	7016	294.6	6804
$265 \cdot 2$	7545	269.8	7462	268.2	7346
243.6	8081	$243 \cdot 2$	8118	238.4	8039
208.2	8902	212.0	8884	200.9	8939
175.2	9892	191.8	9566	$175 \cdot 2$	9746
146.7	11 058	168.8	10.370	144.5	10.863
120.4	12 164	150.0	11 114	120.2	11 902
100.6	12,104	191.0	19 479	109.0	19 796
100.0	19,111	109.9	12,472	96.4	12,120
79·4	13,829	86.8	13,190	78·6	13,272 13,452
		Ni, dien.o	ox(NO ₃),		
Ni, en.c	$(NO_3)_{a}$	- Ĥ	₂ O` 02	Ni ₂ trien,	Cl ₄ ,2H ₂ O
296.0	7363	297.4	7306	297.0	7272
970.9	7776	261.0	7849	267.4	7065
941.0	8889	940.0	8670	949.7	6633
241°0 000.0	0004	019.4	0499	274°1 900.4	0000
222.0	9334 10 404	219.4	9400	209.0	9990
199.9	10,480	199.9	10,308	190.1	11,102
109.8	11,467	100-2	11,522	100.1	13,199
148.8	12,553	140.9	13,189	134.0	15,457
121.6	14,985	108.0	15,803	111.1	18,499
$103 \cdot 2$	16,117	95.8	16,817	89-2	22,103
83.5	17,935	79-9	18,849	79-5	23,984

The compound [Ni₂ trien₃]Cl₄,2H₂O¹⁰ is assumed to contain one bridging and two non-bridging quadridentate trien molecules, so that the two nickel atoms are separated by five single bonds and a distance of probably at least 6 Å.

Magnetic Results.—The experimental susceptibility data for all of the compounds are collected in Table 4. The values listed have been corrected for diamagnetism

⁸ N. F. Curtis, J. Chem. Soc., 1963, 4109.
⁹ R. McCormick and T. N. Waters, unpublished work, quoted by N. F. Curtis, J. Chem. Soc. (A), 1968, 1584.
¹⁰ H. B. Jonassen and B. E. Douglas, J. Amer. Chem. Soc., 1040.

1949, 71, 4094.

using the measured susceptibilities of paa, dhph, and dppn (the same value was used for Me₂dppn and dppl⁻), and Pascal constants ¹¹ for all other atoms and groups, and for temperature-independent paramagnetism using the theoretical expression.⁴ (The t.i.p. was assumed not to be significantly affected by the exchange interaction.) The values of $\mu_{\text{eff}} = 2.828(0.5\chi_{\text{M}}T)^{\frac{1}{2}}$ at 300 and 100° K for all of the compounds are given in Table 1. Above 200°K the susceptibilities conform approximately to the Curie–Weiss law $\chi = C/(T - \theta)$, and the values of θ obtained graphically are also given in Table 1. The susceptibility of a pair of ions in spin triplet, orbital singlet states, with exchange represented by a term $-2JS_1 \cdot S_2$ in the Hamiltonian, is given by equation (1)

$$\chi_{\rm M} = \frac{2N\beta^2 g^2}{kT} \frac{{\rm e}^{-4x} + 5}{{\rm e}^{-6x} + 3{\rm e}^{-4x} + 5} \tag{1}$$

where x = J/kT. The method of least squares was used to find the values of g and J that gave the best fit of this expression to the experimental data. The values obtained are listed in Table 1, together with values of the quantity $R = [\Sigma(\chi_{obs} - \chi_{calc})^2 / \Sigma \chi^2_{obs}]^{\frac{1}{2}}$ as a measure of the agreement between the experimental and calculated curves.

Note that theoretically, $\theta = 1.33 J/k$; however, the value of θ measured just below room temperature is always considerably greater than the true limiting value.

DISCUSSION

The most obvious generalisation that can be made about the results is that all of the compounds in which two Ni²⁺ ions are bridged by a conjugated system show spin-spin interaction, with J/k between -8 and -34° . As far as we are aware, these are the first observations of antiferromagnetic coupling between nickel(II) ions in polynuclear systems, with the exception of the weak interactions ($J/k = ca. -10^{\circ}$) between the terminal Ni atoms of Ni₃ acac₆. ¹² The trien complex shows only very weak exchange (not necessarily intramolecular).

The standard deviation of the J values obtained by the curve-fitting process is in most cases ca. 1%. However, our experience of the variation in J between different packings or different preparations of a given compound, or between different but very closely related compounds (e.g., the di- and tri-hydrates of Ni dhph X₂), suggests that in discussing trends in the actual J values caution must be exercised in attributing significance to any differences less than ca. 10%. Thus, differences in J values within the groups of Me₂dppn, dppl, dhph, and oxalate complexes are probably not really significant. The same is true of the perchlorate and tetrafluoroborate of [Ni₂ paa₃]⁴⁺ (though the difference between these and the iodide is apparently real).

Even allowing for ca. 10% uncertainty in the value of J, however, there are some rather remarkable differences

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between superficially similar compounds in the dppn and Me₂dppn series. Thus, Ni dppn(NO₃)₂,H₂O and Ni dppn(ClO₄)₂,2H₂O have $J/\mathbf{k} = -33$ and -21, and Ni₂ dppn(SO₄)₂,5H₂O and Ni₂(Me₂dppn)(NO₃)₄,2H₂O have $J/\mathbf{k} = -18$ and -30° , respectively. Without detailed knowledge of the actual structures of the molecules we cannot explain these differences; there may possibly be additional effects due to bridging anions, or they may reflect the sensitivity of J to the nature of the non-bridging ligands or to small differences in molecular geometry. One unfortunate consequence is that it is impossible to say, simply by comparing 1:1and 2:1 complexes, whether the value of J depends on the number of superexchange pathways available.

We can, however, attempt to put the various bridging moieties in order of their ability to facilitate spin-spin interaction between Ni²⁺ ions. The order observed (with approximate |J|/k values) is: phthalazine (34) > pyridazine (ca. 30, very variable) > pyrazole (24) > oxalate (22) > azine (10). (The figures refer to a single oxalate ion, three pyridinaldazine molecules, and a pair of ligands in the other cases.) A variety of different structural and electronic factors (bond lengths and angles, ligand basicity, metal-ligand covalency, etc.) could contribute to this variation. The only one that appears to us likely to show a marked trend in the observed direction, at least in the case of the nitrogen ligands, is the electron overlap population of the π -MO's of the bridging system. Thus, if we consider the lowestenergy valence-bond structures (XII), (XIII), and (XIV)



(remembering in the pyrazole case that the electronegativity difference between nitrogen and carbon will be increased by co-ordination), it seems likely that any spin induced in the π -orbital of the left-hand N atom will be transferred into that of the right-hand N atom very efficiently in (XII), less efficiently in (XIII), and much less efficiently (especially if we recall that the azine group is probably twisted) in (XIV).

If the above interpretation of the trend in J values is accepted, we are led to conclude that an important part of the superexchange mechanism in at least some of these complexes must involve excitation of an electron from the t_{2g} into the e_g orbitals of Ni²⁺, the unpaired spins in the t_{2g} orbitals then being coupled together by virtue of their overlap with the π -MO's of the bridging ligand. A comparison of the exchange in the dhph and paa complexes suggests that at least two-thirds of the net antiferromagnetic exchange in the former could be due to this

¹² A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 1968, **7**, 932.

¹¹ B. N. Figgis and J. Lewis, in 'Modern Co-ordination Chemistry,' ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, ch. 6.

process. Such a mechanism represents, of course, a rather high-order effect in terms of perturbation theory, and it is only likely to be important for d^8 and d^9 ions when interaction through σ -bonds is inefficient, e.g., with non-linear polyatomic bridges. The possibility of prior $t_{2g} \rightarrow e_g$ excitation followed by $t_{2g} - t_{2g}$ exchange through a bridging π -system was, in fact, first suggested by Martin and Waterman¹³ to account for the antiferromagnetism of copper(II) formate tetrahydrate, in which the Cu^{2+} ions are linked in chains by bidentate formate ions.

Anderson¹⁴ presented in 1959 a reformulation of the theory of superexchange, in which the basis is a set of 'expanded' metal wave functions derived from the metal orbitals by inclusion of their interaction with the ligand orbitals (in oxides these are Wannier functions, while in a binuclear complex they will be localised MO's). Superexchange is then identified with direct exchange between pairs of these modified orbitals, and will be ferromagnetic if they are orthogonal and antiferromagnetic otherwise. This approach is rather convenient for the description of exchange through polyatomic bridges. Suppose we have a binuclear system of octahedrally co-ordinated ions in which the extended metal orbitals can be divided into mutually orthogonal σ and π sets, based on the e_g and t_{2g} orbitals respectively. In the d^8 case we then have an antiferromagnetic contribution to J, of the form $-b_{\sigma}^2/U$, from the second-order perturbation by the excited state that results from transfer of an electron from one metal to the other $(U = ca. 5 \times 10^4 \text{ cm.}^{-1} \text{ is the energy of this state above})$ the ground state, and the 'transfer integral' b_{σ} is the corresponding off-diagonal matrix element of the total potential). If we now allow the possibility of $t_{2g} \rightarrow e_g$ excitation, we have an additional antiferromagnetic term of the type $-(b_{\pi}^2 b_{te}^2)/\Delta^2(U+\Delta)$, where b_e is the $t_{2g}-e_g$ transfer integral, and $\Delta = 10Dq = ca. 10^4$ cm.⁻¹. For this fourth-order term to predominate we must therefore have relation (2) which is only likely to be true

$$b_{\pi}b_{te}/\Delta > b_{\sigma} \tag{2}$$

if the bridge consists of at least two atoms with considerable π -delocalisation, and Δ is not too large.

EXPERIMENTAL

Apparatus.---Magnetic susceptibilities were measured by the Gouy method at three field strengths, with HgCo(NCS)₄ as calibrant.¹⁵ The magnet current was maintained constant by a servo-stabilised power supply unit designed and built in this Department by Mr. M. C. Drape. The temperature was controlled by a liquid-nitrogen cryostat,¹⁶ and measured with a copper-constantan thermocouple. The measured susceptibility of CuSO₄,5H₂O agreed well with published values ¹⁶ over the range 80-300°K.

¹⁵ B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 1958, 4190.

Diffuse reflectance spectra were recorded between 30,000 and 5000 cm.⁻¹ on a Beckman DK-2 spectrophotometer. I.r. spectra of mulls and pressed KCl discs were recorded on a Perkin-Elmer 457 instrument.

Preparation of Ligands.—The ligands dppn,¹⁷ Me₂dppn,¹⁷ and dhph ¹⁸ were prepared by published methods. Satisfactory analyses for C, H, and N were obtained.

3,5-Di(pyrid-2-yl)pyrazole. Methyl 2-picolinate (prepared in small portions by the reaction of diazomethane with 2-picolinic acid) was condensed with 2-acetylpyridine in the presence of commercial sodium methoxide, by the procedure described by Levine and Sneed ¹⁹ for the acylation of ketones with methyl pyridinecarboxylates. The product was a white solid, m.p. 106-107°, yield ca. 50%. An alternative preparation from ethyl 2-picolinate and 2-acetylpyridine in the presence of sodium ethoxide (cf. dinicotinylmethane²⁰) gave considerably lower yields. The diketone (5.4 g.) was then refluxed for 1.5 hr. with hydrazine hydrate (98-100%, 1.8 g.) in ethanol (70 ml.) and the resulting solution was decolourised with active charcoal and evaporated to 20 ml. The crystals were filtered off and the filtrate diluted to 50 ml. with water, evaporated to 20 ml., and filtered. The combined residues (4.0 g.) were recrystallised from boiling water (2 l.) and dried under vacuum, yield 3.5 g. (66%), white needles, m.p. 188° (Found: C, 70.1; H, 4.6; N, 25.1. C₁₃H₁₀N₄ requires C, 70.2; H, 4.55; N, 25.2%).

Preparation of Complexes.-The nickel complexes of paa,² the nickel ammine hemioxalates,⁸ and the compound Ni₂(trien)₃Cl₄, 2H₂O¹⁰ were prepared as described in the literature. Satisfactory analyses for C, H, N, Ni, and halogen (where present) were obtained in all cases.

Ni dppn(NO_3)₂, H₂O. A filtered solution of Ni(NO_3)₂,-6H₂O (10 mmoles) in a mixture of methanol (AnalaR, 50 ml.) and triethyl orthoformate (30 ml.) at 65° was added with stirring to a filtered solution of dppn (5 mmoles) in a mixture of methanol (125 ml.) and triethyl orthoformate (50 ml.) at 65°. The solution was allowed to stand overnight and the grey-green crystalline precipitate was filtered off, washed with methanol, and dried in air (Found: C, 38.5; H, 2.7; N, 19.4; Ni, 13.4. C₁₄H₁₂N₆NiO₇ requires C, 38.7; H, 2.7; N, 19.3; Ni, 13.55%).

Ni dppn $(ClO_4)_2$, $2H_2O$. A mixture of dppn (2 mmoles) and Ni(NO₃)₂,6H₂O (4 mmoles) in water (40 ml.) was refluxed until the reaction appeared to be complete (ca. 1 hr.). The hot solution was filtered to remove unchanged ligand, and solid sodium perchlorate (20 mmoles) was added. The greygreen precipitate which formed on cooling was filtered off, washed with a little hot water, and dried in air (Found: C, 31.7; H, 2.9; N, 10.6. C₁₄H₁₄Cl₂N₄NiO₁₀ requires C, 31.9; H, 2.6; N, 10.6%).

 $Ni_2 dppn(SO_4)_2, 5H_2O$. A solution of dppn (2 mmoles) in hot ethanol (15 ml.) was added to NiSO₄, 6H₂O (4 mmoles) in hot water (15 ml.), and the green, microcrystalline precipitate was filtered off, washed with hot water and then with ethanol, and dried in air (Found: C, 26.8; H, 3.2; N, 8.7; Ni, 26.7. C₁₄H₂₀N₄Ni₂O₁₃S₂ requires C, 26.6; H, 3.1; N, 8.8; Ni, 26.54%).

Ni₂(Me₂dppn)(NO₃)₄,H₂O,CH₃OH. This was obtained as

¹⁷ W. A. Butte and F. H. Case, J. Org. Chem., 1961, 26, 4690.
 ¹⁸ B.P. 707,337 (1954) (Chem. Abs., 1955, 49, 7606e).
 ¹⁹ R. Levine and J. K. Sneed, J. Amer. Chem. Soc., 1951, 73,

- 5614.
- 20 L. O. Kuick and H. Adkins, J. Amer. Chem. Soc., 1935, 57, 143.

¹³ R. L. Martin and H. Waterman, J. Chem. Soc., 1959, 1359.
¹⁴ P. W. Anderson, Phys. Rev., 1959, 115, 2; see also idem, ch. 2 in 'Magnetism,' vol. 1, ed. G. T. Rado and H. Suhl, Academic Press, New York, 1963.
¹⁵ R. W. Firster and P. S. Nichelm, J. Chem. Soc. 1958, 4100.

¹⁶ B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 1959, 331.

a light green *precipitate* from methanol-triethyl orthoformate solution as described for the dppn complex (Found: C, 29.9; H, 2.9; N, 16.6; Ni, 18.1. $C_{17}H_{20}N_8Ni_2O_{14}$ requires C, 30.1; H, 2.9; N, 16.5; Ni, 17.77%). The presence of methanol was confirmed mass-spectrometrically (CH₃O⁺ at mass 31.0183). On heating in a vacuum at 70° for 2 hr. and then exposing to the air, the green *dihydrate* was obtained (Found: C, 28.8; H, 2.5; N, 17.0. $C_{16}H_{18}Ni_2O_4$ requires C, 28.9; H, 2.7; N, 16.9%).

 $Ni(Me_2dppn)_2(ClO_4)_2, 2H_2O$. This was obtained as a pale green *precipitate* in the same way as the dppn compound (Found: C, 46.9; H, 4.0; N, 13.8. $C_{32}H_{32}Cl_2N_8NiO_{10}$ requires C, 46.9; H, 3.9; N, 13.7%).

Ni dppl $NO_3, 0.5H_2O, 0.5CH_3OH$. This was prepared in the same way as the dppn complex as a pale grey-blue *precipate* (Found: C, 43.8; H, 3.1; N, 19.1; Ni, 15.9. $C_{27}H_{24}N_6O_8Ni_2$ requires C, 44.1; H, 3.3; N, 19.1; Ni, 15.99%).

Ni dppl NO_3, H_2O . The methanol-water solvate was heated in a vacuum at 100° for 3 hr. A red *solid* was obtained, which on exposure to the atmosphere rapidly became pale grey-blue (Found: C, 43.0; H, 3.2; N, 19.1; Ni, 16.5. $C_{28}H_{22}N_6O_8Ni_2$ requires C, 43.1; H, 3.0; N, 19.3; Ni, 16.39%).

Ni dhph $X_2, 3H_2O$ (X = Cl, Br, or I). A solution of the hydrated nickel halide (5 mmoles) in water (15 ml.) was added to a solution of [dhphH]X,0.5H₂O (3 mmoles) in water (15 ml.) in the cold. In the case of the *chloride* and *bromide*, a pale blue precipitate was first formed, which on standing for a few days turned into purple crystals. In the case of the *iodide*, a dark grey-blue crystalline precipitate was formed. The crystals were washed with cold water and dried in air. Large, well-formed crystals can be obtained by starting from more dilute solutions (Found: C, 25.7; H, 4.2; N, 22.4; Cl, 18.9; Ni, 15.8. C₈H₁₆-Cl₂N₆NiO₃ requires C, 25.7; H, 4.3; N, 22.5; Cl, 19.0; Ni, 15.78%. Found: C, 20.8; H, 3.6; N, 18.3; Br, 34.6; Ni, 12.7. C₈H₁₆Br₂N₆NiO₃ requires C, 20.8; H, 3.5; N, 18.2; Br, 34.6; Ni, 12.74%. Found: C, 17.2; H, 2.6; N, 14.8; I, 45.0; Ni, 10.3. $C_8H_{16}I_2N_6NiO_3$ requires C, 17.2; H, 2.9; N, 15.1; I, 45.5; Ni, 10.59%).

Ni dhph $\text{Cl}_2, 2\text{H}_2\text{O}$. This was obtained in the same way except that the solutions were mixed at the boiling point. Blue-grey *crystals* were deposited on cooling (Found: C, 27.5; H, 3.8; N, 23.4; Cl, 19.9; Ni, 16.6. $\text{C}_8\text{H}_{14}\text{Cl}_2\text{N}_6\text{NiO}_2$ requires C, 27.0; H, 3.9; N, 23.6; Cl, 19.9; Ni, 16.57%).

Ni dhph $Cl_2,0.5H_2O$. This was obtained as a hygroscopic green *powder* on heating the higher hydrates in a vacuum at 150° for 5 hr. (Found: C, 29.5; H, 3.2; N, 25.8; Cl, 21.8; Ni, 18.1. $C_{16}H_{22}Cl_4N_{12}Ni_2O$ requires C, 29.2; H, 3.3; N, 25.5; Cl, 21.6; Ni, 17.93%).

Ni dhph $Br_{2,}2H_{2}O$. This was prepared as a grey *powder* by heating the trihydrate in a vacuum at 150° for 5 hr. and exposing the very hygroscopic green product to the air (Found: C, 21.5; H, 3.25; N, 19.1; Br, 35.9; Ni, 13.7. $C_8H_{14}Br_2N_6NiO_2$ requires C, 21.6; H, 3.15; N, 18.9; Br, 36.0; Ni, 13.26%).

Ni dhph Br_2 , H_2O . The trihydrate was heated under a vacuum at 100° for 3 hr., giving a yellow-brown *product* (Found: C, 22.3; H, 2.8; N, 19.6; Br, 37.1. C_8H_{12} - Br_2N_6 NiO requires C, 22.5; H, 2.8; N, 19.7; Br, 37.5%).

Ni dhph I_2, H_2O . The trihydrate was heated under a vacuum at 150° for 5 hr., giving a yellow-brown *product* (Found: C, 18.6; H, 2.3; N, 16.0; I, 48.8. $C_8H_{12}I_2N_6NiO$ requires C, 18.4; H, 2.3; N, 16.1; I, 48.8%).

Analysis.—Microanalyses were determined commercially for C, H, N, Cl, and I. Nickel was determined either by titration with disodium ethylenediaminetetra-acetate, after first destroying the complex by heating with a mixture of concentrated nitric and sulphuric acids; or by ignition in a stream of fluorine at 200° for 3 hr., cooling the pale yellow product in a stream of dry nitrogen, and weighing as NiF₂.

We thank the S.R.C. for a grant (to P. W. B.), the S.R.C. and the Royal Society for grants towards the cost of the magnetic susceptibility apparatus, Dr. B. J. Hathaway for the reflectance spectra, and Dr. P. G. Nelson for the use of a fluorine generator.

[8/1660 Received, November 14th, 1968]