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

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The average magnetic susceptibilities of six binuclear complexes of cobalt(II) between 80 and 400 K are reported. The compounds studied are $Co_2(dhph)_2X_4.nH_2O$ (dhph = 1,4-dihydrazinophthalazine, X = Cl or Br), $Co_2(dppn)_2X_4.nH_2O$ [dppn = 3,6-di-(2-pyridyl)pyridazine, X = NO_3 or ClO_4], $Co_2(dppn)(SO_4)_2.5H_2O$, and $Co_2(Me_2dppn)(NO_3)_4.2CH_3OH$ [Me_2dppn = 3,6-di-(6-methyl-2-pyridyl)pyridazine]. These compounds exhibit weak antiferromagnetic exchange, and the values of the effective isotropic exchange parameter $\mathcal{J}$ are estimated, making allowance for spin–orbit coupling and the effects of orbital reduction and axial distortion parameters. The values of $\mathcal{J}$ are compared with those of the analogous nickel complexes reported earlier, and it is concluded that the t_{2g} spin of Co^{2+} probably makes a ferromagnetic contribution. The exchange interaction is analysed in a one-electron orbital basis, leading to an anisotropic form for the exchange parameter. The average susceptibility data do not distinguish between the isotropic and anisotropic models, however, and the precise identity of the orbitals responsible for the ferromagnetic contribution remains uncertain.

IN an earlier paper we described some binuclear nickel complexes of ligands containing a pair of adjacent nitrogen atoms, and interpreted their magnetic behaviour in terms of a superexchange interaction *via* the N–N bridge.[1] Three of the ligands, 1,4-dihydrazinophthalazine (dhph), 3,6-di-(2-pyridyl)pyridazine (dppn), and 3,6-di-(6-methyl-2-pyridyl)pyridazine (Me_2dppn), gave compounds with cobalt(II) that appeared to have the same structures as their nickel analogues, and thus offered an opportunity to compare the superexchange behaviour of nickel and cobalt in similar environments. We now report the magnetic properties of these cobalt complexes, and use them to pursue the question of the mechanism of superexchange in systems of this type, particularly the effect of the unpaired spin in the t_{2g} orbitals of Co^{2+}. In doing this we shall have to take account of the orbital momenta of the ions, since they are in approximately octahedral co-ordination in all these complexes. A

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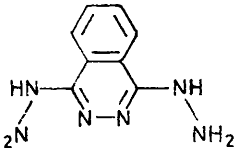
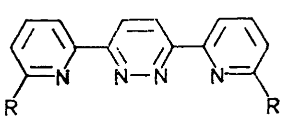
[1] Part I, P. W. Ball and A. B. Blake, *J. Chem. Soc.* (*A*), 1969, 1415.

preliminary account of these results has appeared elsewhere.[2]



dhph



R = H, dppn
R = Me, Me_2dppn

RESULTS

As before, we begin by presenting the evidence for binuclear structures, analogous to those previously assigned to the nickel complexes.

Spectra and Structures of the Complexes.—The compounds, which are listed in Table 1, are orange, paramagnetic, crystalline solids which darken slowly in air (rapidly when moist). The diffuse reflectance spectra of compounds (III)—(VI) show a broad, slightly asymmetric band centred between 9000 and 11 000 cm^{-1}, assigned to the $^4T_{1g} \longrightarrow {}^4T_{2g}$ transition of Co^{2+} in pseudo-octahedral symmetry, and up to three weaker bands between 18 000 and 24 000 cm^{-1}, appearing as shoulders on an intense u.v. band, which probably correspond to the transitions to $^4A_{2g}$ and $^4T_{1g}(P)$. [The sensitivity of compounds (I) and (II) to oxidation prevented satisfactory spectra from being obtained in these cases.]

TABLE 1

The compounds studied and some magnetic properties

Number	Compound	μ_{eff} (300 K)	μ_{eff} (100 K)	$-\theta$/K
(I)	$Co_2(dhph)_2,Cl_4,5H_2O$	4·44	3·99	67
(II)	$Co_2(dhph)_2Br_4,6H_2O$	4·45	3·93	58
(III)	$Co_2(dppn)_2(NO_3)_4,2H_2O$	4·43	3·97	50
(IV)	$Co_2(dppn)_2(ClO_4)_4,6H_2O$	4·24	3·89	40
(V)	$Co_2(dppn)(SO_4)_2,5H_2O$	4·53	4·21	35
(VI)	$Co_2(Me_2dppn)(NO_3)_4,2CH_3OH$	4·24	3·94	45

The magnetic properties of all six compounds suggest the presence of a weak exchange interaction, in that the values of the Weiss constant θ (Table 1) are considerably larger than those commonly observed in mononuclear cobalt(II) complexes.* These compounds were prepared in a similar manner to the corresponding nickel complexes, and have similar formulae (differing by a molecule of solvent in some cases). The evidence for formulating both series of compounds as binuclear can be summarised as follows.

(i) The stoicheiometries and electronic absorption spectra of the nickel complexes are most simply accounted for by binuclear structures, and their magnetic behaviour between 80 and 300 K agrees closely with that predicted for pairs of $^3A_{2g}$ ions with a weak antiferromagnetic exchange interaction (J *ca.* -40 cm^{-1}).[1]

(ii) The compound $Ni(dhph)Cl_2,3H_2O$ has been shown by X-ray crystal-structure analysis to contain the centrosymmetric binuclear cation $[Ni_2(dhph)_2(H_2O)_4]^{4+}$, Figure 1.[4] Comparison of single-crystal X-ray diffraction photographs of the $hk0$ and $0kl$ levels of this compound and its cobalt analogue, compound (I), shows conclusively that the two are isomorphous.

(iii) X-Ray powder photographs show that compound (III) is isomorphous with its nickel analogue.

(iv) The i.r. spectra of compounds (I)—(V) resemble those of their nearest nickel analogues to a degree that we believe reflects close similarities between the respective structures.† Thus, the spectra of compounds (III) and (V) between 4000 and 250 cm^{-1} are virtually identical with those of the corresponding nickel compounds, and the resemblance is very close in the cases of (I), (II), and (IV). The spectrum of (VI) is sufficiently different from that of its nickel analogue to prevent a definite conclusion, though the differences can be accounted for partly by the different solvation.

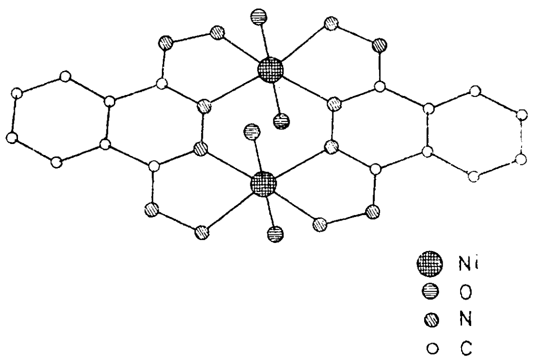


FIGURE 1 Structure of $[Ni_2(dhph)_2(H_2O)_4]^{4+}$ (ref. 4). The chloride of this ion is isomorphous with compound (I)

Taking the evidence as a whole, we feel reasonably confident in assigning binuclear structures with N–N bridges to all the complexes of cobalt and nickel in this study.

Magnetic Results and Interpretation.—The experimental susceptibility data for the finely powdered solids between 80 and 400 K are collected in Table 2.‡ The values listed have been corrected for diamagnetism as before,[1] and for temperature-independent paramagnetism (t.i.p.) as described in Appendix I. The t.i.p. correction is small (less than 2%), but we include it so that the cobalt and nickel results will be strictly comparable. The values of the effective magnetic moment $\mu_{eff} = 2{\cdot}828\ (\chi_a T)^{\frac{1}{2}}$ at 300 and 100 K (where χ_a is the susceptibility per mole of Co atoms)

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* Of 23 magnetically dilute, octahedral, cobalt(II) compounds whose θ values in the range 80—300 K are listed by König,[3] 22 have θ between -11 and -36 K, with a mean of -23 K. (The curious exception is $CoSeO_4,6H_2O$, -64 K.) The presumably mononuclear complex $Co(Me_2dppn)_2(ClO_4)_2,3H_2O$ has $\theta = -26$ K.

† We are aware that similarity of the i.r. spectra of such complex compounds is not an infallible indication of similarity of their structures, but we feel that it is very unlikely that such close resemblances as are observed here could arise from grossly different co-ordination of the ligands in cobalt and nickel compounds with analogous formulae. It is worth mentioning that the i.r. spectrum of $Co_2(dppn)_2(NO_3)_4,2H_2O$ is quite different from (and indeed much simpler than) that of $Mn(dppn)_2(NO_3)_2$, which is known from a crystal-structure analysis to be mononuclear, with bidentate NO_3^- and only one half of each dppn molecule co-ordinated.[5]

‡ Magnetic susceptibilities are given in this paper in the c.g.s. electromagnetic system, in the interest of uniformity with Part I. To convert to m^3 mol^{-1} in SI, the values given should be multiplied by $4\pi \times 10^{-6}$.

[2] J. E. Andrew, P. W. Ball, and A. B. Blake, *Chem. Comm.*, 1969, 143.

[3] Landolt-Bornstein, New Series, Group II, Volume 2, 'Magnetic Properties of Co-ordination and Organometallic Transition Metal Compounds,' by E. König, Springer, Berlin, 1966.

[4] J. E. Andrew and A. B. Blake, *J. Chem. Soc.* (*A*), 1969, 1408.

[5] A. B. Blake and L. R. Fraser, unpublished work.

are given in Table 1, together with values of the Weiss constant θ estimated graphically as before.[1]

In interpreting the magnetic data to obtain estimates of the exchange parameters, we are confronted with a much more difficult problem than in the nickel case. In both cases the metal ions are in approximately octahedral co-ordination with a tetragonal distortion; but the $^3A_{2g}$ ground term of Ni^{2+} is split (to first order) only by exchange, whereas the $^4T_{1g}$ ground term of Co^{2+} is split by both spin–orbit coupling and the low-symmetry field even in the absence of exchange, and the contribution of these effects to the temperature dependence of the magnetic moment must be allowed for before a comparison of exchange in the nickel and cobalt cases is possible. A further complication which arises in the cobalt case is that the three 't_{2g}' orbitals contain only one unpaired spin, and since in the symmetry of a binuclear complex these three orbitals cannot be equivalent, the strength of the exchange will depend on which one is occupied on each ion. This not only contributes substantially to the magnetic anisotropy of the complex, but also means that more than one exchange parameter is required to describe its magnetic properties.

TABLE 2

Magnetic susceptibilities ($cm^3\ mol^{-1}$, after correction for t.i.p. and diamagnetism as described in the text)

T/K	$10^5\chi$
$Co_2(dhph)_2Cl_4,5H_2O$	
296·5	1701
273·0	1818
241·9	2006
213·8	2193
187·2	2434
160·0	2755
137·8	3088
102·8	3912
92·4	4163
80·5	4518
$Co_2(dppn)_2(ClO_4)_4,6H_2O$	
369·6	1239
360·2	1280
345·5	1322
328·0	1388
313·8	1446
299·2	1498
292·8	1534
266·1	1654
238·2	1825
212·2	2018
183·8	2286
149·3	2729
120·4	3302
95·3	3910
77·9	4554
$Co_2(dhph)_2Br_4,6H_2O$	
381·6	1327
364·0	1383
345·3	1456
322·7	1549
310·2	1598
295·5	1668
294·5	1679
271·3	1795
238·8	1987
215·0	2146
190·6	2369
156·5	2767
136·2	3065
116·2	3471
98·0	3903
77·2	4406
$Co_2(dppn)(SO_4)_2,5H_2O$	
361·8	1455
347·1	1519
330·0	1570
320·6	1617
300·0	1719
275·3	1884
242·2	2090
210·0	2355
178·8	2679
144·0	3255
112·8	4002
95·2	4607
86·4	4952
$Co_2(dppn)_2(NO_3)_4,2H_2O$	
408·2	1235
395·1	1281
376·0	1336
362·1	1370
345·4	1437
327·8	1505
313·1	1582
297·4	1651
296·0	1663
270·8	1768
244·4	1941
216·5	2124
189·2	2348
167·4	2619
143·6	2963
122·0	3367
98·4	3986
79·2	4510
$Co_2(Me_2dppn)(NO_3)_4,2CH_3OH$	
296·8	1666
275·6	1778
251·8	1929
236·4	2050
188·2	2413
157·0	2806
138·2	3010
116·1	3495
97·4	3933
86·8	4211

Clearly, the magnetic behaviour of a binuclear cobalt(II) complex can be interpreted at several levels of approximation, and it would be useful to know how the results of these compare. We shall examine three models. The simplest ignores the effects of orbital degeneracy, and is equivalent to assuming that there is a distortion from octahedral symmetry large enough to split the $^4T_{1g}$ terms by an energy $\gg$ $\mathbf{k}T$, with the orbital singlet levels lowest; the spin states are assumed to be coupled by an isotropic Heisenberg exchange interaction. The second model starts with the cubic-field $^4T_{1g}$ terms, and assumes them to be perturbed by spin–orbit coupling and an isotropic exchange interaction; a small axial distortion can also be included if necessary. Finally, in the third model the orbital dependence of the individual exchange integrals is recognised, leading to an anisotropic (but, in a centrosymmetric complex, still symmetric) exchange operator.

(1) *Ions in orbital singlet states.* As in the nickel case,[1] the observed decrease in the magnetic moment with decreasing temperature is ascribed solely to an exchange term $-2\mathscr{J}\mathbf{S}_A \cdot \mathbf{S}_B$ in the Hamiltonian. The susceptibility of the pair of ions is given by equation (1), where $x = \mathscr{J}/\mathbf{k}T$. This

$$\chi_M = \frac{2N\mu_B^2g^2}{\mathbf{k}T}\,\frac{e^{-10x} + 5e^{-6x} + 14}{e^{-12x} + 3e^{-10x} + 5e^{-6x} + 7} \qquad (1)$$

expression was fitted to the experimental data for compounds (I)—(VI) by the method of least squares, giving the values for g and $\mathscr{J}$ shown in Table 3, column (1).* Values of the function $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}^2]^{\frac{1}{2}}$ are also listed, as a measure of the discrepancy between the experimental and calculated curves.

(2) *Ions in $^4T_{1g}$ states with isotropic exchange.* Several authors have recently given attention to this type of problem.[6-9] Lines has discussed the effect of spin–orbit

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* Energies involved in thermal equilibria are given here in units of **k**K, where **k** is Boltzmann's contant, equal to 8·310 J K^{-1}.

[6] J. Kanamori, *Progr. Theoret. Phys.* (*Japan*), 1957, **17**, 177.

[7] T. Nakamura and N. Uryû, *J. Phys. Soc. Japan*, 1956, **11**, 760; A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Metal Ions,' Oxford, Clarendon, 1970.

[8] M. E. Lines, *J. Chem. Phys.*, 1971, **55**, 2977.

[9] (*a*) O. Kahn, *J. Chim. Phys.*, 1973, **70**, 392; (*b*) J. C. Bernier and O. Kahn, *Chem. Phys. Letters*, 1973, **19**, 414.

coupling on the magnetic properties of two to four exchange-coupled Co^{2+} ions, using an ingenious hybrid approximation which combines an exact spin Hamiltonian for the lowest Kramers doublets with a molecular-field representation of exchange in the upper levels of the ground multiplet.[8] For a cluster of only two Co^{2+} ions, however, a perturbation treatment of the complete $^4T_{1g} \times {}^4T_{1g}$ manifold is practicable, and should be more accurate. We use a computer program which does this for the general ^{2S+1}T case ($S = \frac{1}{2}$, 1, $\frac{3}{2}$, or 2).

The effect of spin–orbit coupling can be represented by the operator $\mathscr{H}_{LS} = -\lambda(\mathbf{L}_A \cdot \mathbf{S}_A + \mathbf{L}_B \cdot \mathbf{S}_B)$ acting on product functions derived from pseudo-^4P states of the ions A and B.[10] This operator must, however, be modified to take account of mixing of metal and ligand wavefunctions as a result of covalency (which causes the true matrix elements of $\mathbf{L}$ to be smaller than those obtained using pure d wavefunctions), and mixing of the strong-field determinantal wavefunctions as a result of interelectronic repulsion. The first can be allowed for by introducing an orbital reduction factor k as an empirical parameter,[11] and the second by multiplying $\mathbf{L}$ by another numerical factor A, whose value lies between 1·0 and 1·5 and can be estimated independently from spectroscopic data.[12] From the reflectance spectra of compounds (3)—(5) we calculate[13] $A = 1{\cdot}39 \pm 0{\cdot}02$ (see Appendix I). The free-ion spin–orbit coupling constant λ is thus replaced by $kA\lambda$, and the magnetic moment operator becomes $-kA\mathbf{L} + 2\mathbf{S}$. Note that the values of k are not necessarily the same in these two expressions, but we assume them to be equal; we also ignore the possibility of anisotropy in k, A, or λ. For ^4F of the free Co^{2+} ion, $\lambda/\mathbf{k} = -256$ K.[10]

TABLE 3

Some derived magnetic parameters

Compound number	(1) g	(1) $-\mathscr{J}/\mathbf{k}$K	(1) 10^2R	(2) k	(2) $D/\mathbf{k}$K	(2) $-\mathscr{J}/\mathbf{k}$K	(2) 10^2R	$^4\mathscr{J}_{Ni}/{}^9\mathscr{J}_{Co}$ [a]
(I)	2·39	10·6	1·15	1·03	2100	7·7	1·11	1·9
(II)	2·41	11·9	0·94	1·04	2100	9·0	0·86	1·7
(III)	2·38	10·6	1·29	0·79	1100	7·6	1·21	2·0
(IV)	2·26	8·2	0·85	0·50	500	6·0	1·51	1·6
(V)	2·41	7·5	0·82	0·65	250	3·0	1·79	2·6
(VI)	2·41	11·6	1·16	0·65	250	8·5	1·66	1·6

[a] $\mathscr{J}_{Co}$ from Section (2) of this Table, $\mathscr{J}_{Ni}$ from ref. 1.

According to the structures assigned to the nickel complexes,[1] the donor-atom set in each compound is either *trans*-N_4O_2 or *cis*-N_2O_4, and the ligand field may therefore deviate considerably from cubic, though retaining roughly tetragonal symmetry about the z-axis in the co-ordinate system of Figure 2. An axial distortion in the z-direction can be represented approximately (provided we remain within the $^4T_{1g} \times {}^4T_{1g}$ subspace) by the operator-equivalent $\mathscr{H}_{LL} = D(L_{zA}{}^2 + L_{zB}{}^2 - 4/3)$, where D is the splitting of the individual ion T-term by the axial field, and is positive if the orbital singlet lies lowest. Since we need to keep the number of parameters down, we have endeavoured to estimate D for each compound independently in the following way. In a spectroscopic study of a series of isomorphous tetragonal complexes of the type ML_4X_2 (L = 3-methylpyrazole, X = Cl, Br, I, or NO_3), Reedijk found that the ratio D_{Co}/D_{Ni} varied between 0·31 and 0·37, with a mean of 0·35.[14] We therefore take D positive and equal to 0·35 times the splitting of the $^3T_{1g}(F)$ term of the analogous nickel complex, determined from its reflectance spectrum[1] (assuming in each case that the ligand field is weakest along the tetragonal axis). The estimated values of D are shown in Table 3. [For compounds (V) and (VI) the splitting was not resolved in the spectrum of the nickel analogue, so that in these two cases the small value assigned to D is simply a reasonable guess.]

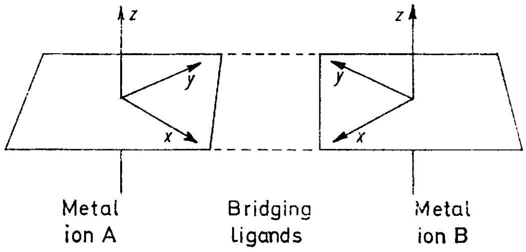

FIGURE 2 Co-ordinate system to which the orbitals of the metal ions are referred

The complete perturbation is thus represented by the Hamiltonian (2), and the quantities to be determined by curve fitting to the experimental data are k and $\mathscr{J}$. The

$$\begin{aligned}\mathscr{H}_I &= D(L_{zA}{}^2 + L_{zB}{}^2 - 4/3) - \\ &\quad kA\lambda(\mathbf{L}_A \cdot \mathbf{S}_A + \mathbf{L}_B \cdot \mathbf{S}_B) - 2\mathscr{J}\mathbf{S}_A \cdot \mathbf{S}_B \\ &= \mathscr{H}_{LL} + \mathscr{H}_{LS} + \mathscr{H}_{SS} \qquad (2)\end{aligned}$$

method of calculating the susceptibility is described in Appendix III. Since the dependence of χ on k and $\mathscr{J}$ cannot be expressed analytically, the usual method of least squares is not applicable, and a trial-and-error fit is necessary. k and $\mathscr{J}$ were therefore varied by small amounts, and contours of the mean squared deviation were plotted until a minimum was located for each compound. The results are shown in Table 3, column (2).*

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* It must be emphasised that equally good fits can often be obtained with considerably different assumed values of D. We find, however, that with k, D, and $\mathscr{J}$ as parameters, any constraint on D is accommodated mainly in the value of k, and *vice versa*, the best-fit value of $\mathscr{J}$ being comparatively insensitive to other parameters. It is clear that too much significance should not be attached to the values of k listed in Table 3.

[10] J. S. Griffith, 'The Theory of Transition-Metal Ions, Cambridge, 1961.

[11] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

[12] B. N. Figgis, 'Introduction to Ligand Fields,' Interscience, 1966, p. 270.

[13] B. N. Figgis, *J. Chem. Soc.* (*A*), 1968, 2086.

[14] J. Reedijk, *Rec. Trav. chim.*, 1970, **89**, 993.

(3) *Ions in $^4T_{1g}$ states with anisotropic exchange.** The spin-dependent part of the energy of interaction between two many-electron ions A and B was shown by Heisenberg and Dirac to have the form (3), where the summation is over the electrons i of ion A and j of ion B. When A and B

$$\mathscr{H}_{\mathrm{SS}} = -2\sum_{i,j} J(i,j)\mathbf{s}_{\mathrm{A}}(i) \cdot \mathbf{s}_{\mathrm{B}}(j) \qquad (3)$$

are in orbitally non-degenerate states, (3) reduces to the usual exchange operator $-2\mathscr{J}\mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}}$, where $\mathbf{S}$ is the total spin of the ion and $\mathscr{J}$ is a constant. But, as Van Vleck pointed out some years ago,[15] when the ions have orbital degeneracy, the $J(i,j)$ will be matrices connecting the orbital wavefunctions of the electrons, and the transformation of (3) to the form $-2\mathscr{J}\mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}}$ will then in general result in $\mathscr{J}$ being anisotropic and dependent on the orbital states of the ions. A detailed and general discussion of this problem has been given by Levy,[16] but because of the large number of parameters in the full theory, the possibility of anisotropic exchange is often ignored.[8,9] Nevertheless, it is useful to return to (3) if we wish to understand in a qualitative way how the exchange interaction differs in the nickel and cobalt complexes. We shall take up later the question of whether the orbital dependence of $\mathscr{J}$ can in fact be estimated from powder data.

The transformation of (3) to a basis of atomic states is carried out by elementary methods in Appendix II for the d^8 and d^7 cases. For two Ni^{2+} ions we find that (3) is equivalent to the spin operator (4) acting on the states $|M_{\mathrm{SA}}\rangle|M_{\mathrm{SB}}\rangle$ of the direct product $^3A_{2g} \times {}^3A_{2g}$, where θ and ε are real orbitals derived from the d_{z^2} and $d_{x^2-y^2}$ orbitals,

$$\begin{aligned}\mathscr{H}_{\mathrm{SS}} &= -2[J(\theta\theta) + 2J(\theta\varepsilon) + J(\varepsilon\varepsilon)]\mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}}/4S^2 \\ &= -2\mathscr{J}\mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}} \end{aligned} \qquad (4)$$

respectively, of a single metal ion in the co-ordinate system of Figure 2, and the exchange integrals $J(\phi_{\mathrm{A}}\phi_{\mathrm{B}})$ are the diagonal matrix elements $\langle\phi_{\mathrm{A}}\phi_{\mathrm{B}}|J|\phi_{\mathrm{A}}\phi_{\mathrm{B}}\rangle$ of the orbital part of the exchange interaction (3). $\mathscr{J}$ is thus identified with the 'average' exchange integral $\bar{J}(ee) = [J(\theta\theta) + 2J(\theta\varepsilon) + J(\varepsilon\varepsilon)]/4$; as far as we are aware, there is no empirical way in which the orbital integrals $J(\phi_{\mathrm{A}}\phi_{\mathrm{B}})$ can be evaluated separately.

In the cobalt case, the ground term $^4T_{1g}$ is a mixture of $t_{2g}{}^4e_g{}^3$ and $t_{2g}{}^5e_g{}^2$ functions. Neglecting the $t_{2g}{}^4e_g{}^3$ contribution (which, according to spectroscopic evidence, is only *ca.* 6%), we find in Appendix II that (3) is equivalent to the spin operator (5) acting on the states $|M_{\mathrm{LA}}M_{\mathrm{SA}}\rangle|M_{\mathrm{LB}}M_{\mathrm{SB}}\rangle$ of the direct product $^4T_{1g} \times {}^4T_{1g}$, where L (= 1) is the

$$\mathscr{H}_{\mathrm{SS}} = -2\mathscr{J}(M_{\mathrm{LA}},M_{\mathrm{LB}})\mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}} \qquad (5)$$

'effective' orbital angular momentum quantum number. The three distinct exchange parameters $\mathscr{J}(M_{\mathrm{LA}},M_{\mathrm{LB}})$ are given by (6), in which ξ, η, and ζ are the t_{2g} orbitals, $\bar{J}(ee)$

$$\begin{aligned}\mathscr{J}(0,0) &= [4\bar{J}(ee) + 4\bar{J}(e\zeta) + J(\zeta\zeta)]/9 \\ \mathscr{J}(1,0) &= [4\bar{J}(ee) + 2\bar{J}(e\zeta) + 2\bar{J}(e\xi) + J(\zeta\xi)]/9 \\ \mathscr{J}(1,1) &= [4\bar{J}(ee) + 4\bar{J}(e\xi) + \tfrac{1}{2}J(\xi\xi) + \tfrac{1}{2}J(\xi\eta)]/9 \end{aligned} \qquad (6)$$

is defined as before, and $\bar{J}(e\phi) \equiv \frac{1}{2}[J(\theta\phi) + J(\varepsilon\phi)]$ ($\phi = \zeta$ or ξ).† Note that (6) contains eleven distinct orbital exchange integrals [*cf.* equation (15), Appendix II], and again there is no way in which they can be evaluated individually, even if the three $\mathscr{J}$'s can be experimentally determined.

If we assume that $\bar{J}(ee)$ will not be greatly different in the nickel and cobalt cases, the main differences between $\mathscr{J}$ for nickel and the $\mathscr{J}(M_{\mathrm{LA}},M_{\mathrm{LB}})$ for cobalt, apart from the anisotropy of the latter, are the factor 4/9 arising from the different total spins, and the addition of terms of the type $J(\phi_{\mathrm{A}},\phi_{\mathrm{B}}')$, $\phi' \neq \phi$, in the cobalt case. Such terms are likely to be positive, *i.e.* ferromagnetic, in nature,[19] and their net effect might be expected to outweigh that of the additional terms $J(\zeta\zeta)$ and $J(\xi\xi)$ (whose signs are probably negative but which are statistically less important), making all three $\mathscr{J}$'s less negative than in the absence of t_{2g} contributions. If the t_{2g} orbitals made no contribution, we should, of course, have a single isotropic exchange parameter $\mathscr{J} = (4/9)\bar{J}(ee)$.

To determine whether average susceptibility measurements over the range 80—400 K can reveal anything about the orbital dependence of exchange in complexes of the type we are concerned with, we selected the data for compound (III). With $D/\mathbf{k}$ equal to 1100 K and k equal to the value estimated by using the isotropic model, the values of $\mathscr{J}(0,0)$, $\mathscr{J}(1,0)$, and $\mathscr{J}(1,1)$ were systematically varied over the range −14 to +2 K in an effort to find a minimum in the value of the discrepancy index R. Not unexpectedly, the fit, though quite sensitive to the average, was found to be rather insensitive to the individual values of the $\mathscr{J}$'s; low values of R were confined not to a point in the three-dimensional $\mathscr{J}$-space, but to a plane defined approximately by $[\mathscr{J}(0,0) + \mathscr{J}(1,0) + 1{\cdot}5\,\mathscr{J}(1,1)]/\mathbf{k} = -26{\cdot}4$ K. The best fit had $\mathscr{J}(0,0)/\mathbf{k}$ *ca.* −12, $\mathscr{J}(1,0)/\mathbf{k}$ *ca.* −10, and $\mathscr{J}(1,1)/\mathbf{k}$ *ca.* −3 K, with $R = 0{\cdot}0117$, but almost equally good fits could be obtained with considerably different values, the only consistent observation being an apparent preference for $\mathscr{J}(1,1)$ to be less negative than $\mathscr{J}(0,0)$ or $\mathscr{J}(1,0)$. The individual estimation of the three exchange parameters in compounds of this type must evidently await single-crystal magnetic measurements.

DISCUSSION

We have used three models to interpret the magnetic properties of the binuclear cobalt(II) complexes. The first, in which the temperature dependence of the mag-

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* The authors are indebted to a referee of the original version of this paper for drawing their attention to the work of Levy [16] on anisotropic exchange.

† Actually, both diagonal and off-diagonal integrals $\langle\phi'_{\mathrm{A}}\phi'_{\mathrm{B}}|J|\phi_{\mathrm{A}}\phi_{\mathrm{B}}\rangle$ appear in the expression for the exchange energy, and there is no theoretical justification for assuming that the off-diagonal terms are negligible. However, of the 625 integrals (for $l = 2$), Levy [16] has shown that 145 are distinct even when the two ions are related by a centre of inversion, and although the number will be reduced further in D_{2h} symmetry, it is clear that some very drastic assumptions are necessary before we have a model that can be related to experiment. Copland and Levy,[17] in a discussion of direct exchange between Co^{2+} ions, chose for practical reasons to ignore the off-diagonal integrals, and Barraclough and Gregson [18] have done the same in their treatment of $Ti_2Cl_9{}^{3-}$. We here assume that the matrix of J is diagonal in a basis of real d-orbitals (the results are essentially the same if complex orbitals are used), with the aim of interpreting our results in terms of those diagonal elements that seem likely to be most important, but we must emphasise that this is to be regarded at present more as a simplifying convention than a justifiable approximation. Note, however, that $\bar{J}(ee)$ is necessarily diagonal.

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[16] P. M. Levy, *Phys. Rev.*, 1969, **177**, 509.

[17] G. M. Copland and P. M. Levy, *Phys. Rev. B.*, 1970, **1**, 3043.

[18] C. G. Barraclough and A. K. Gregson, *J.C.S. Faraday II*, 1972, 177.

[19] P. W. Anderson, in 'Magnetism,' eds. G. T. Rado and H. Suhl, vol. I, Academic Press, 1963, ch. 2.

netic moment is assumed to be due entirely to exchange, is obviously inappropriate: the effective magnetic moment of an octahedral cobalt(II) complex normally decreases over the temperature range 400—80 K, as a result of the splitting of the ${}^4T_{1g}$ ground term by spin–orbit coupling and distortion,[3] and in neglecting these effects we must inevitably overestimate the importance of any antiferromagnetic exchange interaction. We were interested to know the extent of this overestimation, which can be seen by comparing the results obtained by using models (1) and (2) in Table 3. (Note that the spin-only model gives quite a good fit to the data, probably because the orbital effects are partly accommodated in the false parameter g.)

The second model takes the spin–orbit coupling and distortion into account, and leads to values of the effective isotropic exchange parameters that should be much more realistic. Unfortunately, in doing so it introduces two new parameters, both of rather uncertain value, so that the accuracy of the results will not be high. We assume a possible error of $\pm 10\%$ in $\mathscr{J}$, arising from these uncertainties.

In the third model, we have attempted to include the orbital dependence of the exchange resulting from the inherently low symmetry of a binuclear complex, but we find that our powder data are barely capable of distinguishing this from an isotropic interaction. We therefore use the results of model (2) in comparing the strengths of exchange in the binuclear cobalt and nickel complexes discussed in this paper and Part I.[1]

From Table 3 it may be seen that the ratio $(4/9)\mathscr{J}_{\mathrm{Ni}}/\mathscr{J}_{\mathrm{Co}}$ for the six pairs of compounds lies between 1·6 and 2·6, with five of the values being between 1·6 and 2·0. Because of the experimental uncertainties in the $\mathscr{J}$'s it is doubtful that the deviations from the mean of 1·9 are of much significance, and we conclude that the trends in $\mathscr{J}$ from one complex to another for a given metal are largely the result of structural variations that affect the interaction rather similarly for cobalt and nickel. As was noted previously, we are not able to explain these variations in $\mathscr{J}$.

The value of $1{\cdot}9 \pm 0{\cdot}3$ for $(4/9)\mathscr{J}_{\mathrm{Ni}}/\mathscr{J}_{\mathrm{Co}}$ may be compared with the value of *ca.* 1·3 found in the oxides.* If the t_{2g} electrons of Co^{2+} made no net contribution to the exchange, this ratio would be equal to $\bar{J}(ee)_{\mathrm{Ni}}/\bar{J}(ee)_{\mathrm{Co}}$. Nesbet has calculated a theoretical value of *ca.* 1·6 for the latter ratio in the oxides,[22] and although the approximations involved in this calculation have been questioned by Anderson,[23] both authors' theories seem to indicate that this ratio should not be strongly dependent on the nature of the ligands. (The e_g contribution to $\mathscr{J}$ by Anderson's mechanism is $2b^2/U$, where b is roughly equal to one third of the ligand-field splitting and U is the energy required to transfer an electron from one cation to the other.[24]) It thus seems that the t_{2g} contribution to the exchange in our compounds is considerably more positive than in CoO, and although we cannot be certain about the actual sign of the contribution in either case, it seems likely that it is in fact ferromagnetic in the binuclear complexes.

The major ferromagnetic terms in equation (6) are probably $4\bar{J}(e\zeta)$ and $4\bar{J}(e\xi)$. There is a slight indication that $\mathscr{J}(1,1)$ is less negative than $\mathscr{J}(0,0)$ or $\mathscr{J}(1,0)$, which would suggest that the $d\pi$ orbitals (ξ and η) provide the strongest ferromagnetic contributions, perhaps through the azine π-system. In the absence of magnetic anisotropy information, however, further speculation is unfruitful.

EXPERIMENTAL

Magnetic susceptibilities were measured on finely powdered samples by the Gouy method as described previously.[1] Diffuse reflectance spectra were recorded between 5000 and 30 000 cm^{-1} on a Beckman DK2 spectrophotometer.

Preparation of Complexes.—The methods were similar to those used for the nickel complexes,[1] except for the compounds with dihydrazinophthalazine, which are easily oxidised and were prepared using air-free solutions in an atmosphere of oxygen-free nitrogen and subsequently manipulated in a nitrogen-filled glove box. Microanalysis for C, H, N, Cl, and Br was performed commercially, with the results: (I), Found: C, 26·3; H, 4·1; N, 23·2; Cl, 19·2. $C_{16}H_{30}Cl_4Co_2N_{12}O_{15}$ requires C, 26·4; H, 4·1; N, 23·0; Cl, 19·4. (II), Found: C, 20·9; H, 3·5; N, 18·5; Br, 34·5. $C_{16}H_{32}Br_4Co_2N_{12}O_{16}$ requires C, 20·8; H, 3·5; N, 18·2; Br, 34·6. (III), Found: C, 38·7; H, 2·7; N, 19·3. $C_{28}H_{24}Co_2N_{12}O_{14}$ requires C, 38·7; H, 2·7; N, 19·3. (IV), Found: C, 30·8; H, 3·0; N, 10·2; Cl, 13·2. $C_{28}H_{52}Cl_4Co_2N_8O_{22}$ requires C, 30·8; H, 2·9; N, 10·2; Cl, 13·0. (V), Found: C, 26·6; H, 3·2; N, 8·6. $C_{14}H_{20}Co_2N_4O_{13}S_2$ requires C, 26·6; H, 3·1; N, 8·8. (VI), Found: C, 31·3; H, 3·1; N, 16·1. $C_{18}H_{22}Co_2N_8O_{14}$ requires C, 31·2; H, 3·2; N, 16·2%.

APPENDIX I

Configuration Mixing and T.I.P. for Co²⁺ in an Octahedral Field.—The ${}^4T_1$ wavefunctions of a d^3 or d^7 ion in cubic symmetry have the form (7), where $a^2 + b^2 = 1$, $a/b = (10Dq + 9B + R)/12B$, and $R^2 = (10Dq)^2 + 180\ BDq + (15B)^2$, the separation of the ${}^4F$ and ${}^4P$ terms in the limit

$$\begin{aligned} |T_1{}^+\rangle &= a|t_2{}^2eT_1\rangle + b|t_2e^2T_1\rangle \\ |T_1{}^-\rangle &= b|t_2{}^2eT_1\rangle - a|t_2e^2T_1\rangle \end{aligned} \qquad (7)$$

$Dq = 0$ being $15B$. The values of Dq and B for an octahedral cobalt(II) complex may be calculated from spectroscopic data by equations (8), where E_1, E_2, and E_3 are the

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* According to the simple molecular-field theory, the Néel temperature for the NaCl structure with spin ordering of the second kind is given by $T_{\mathrm{N}} = -4\ \mathscr{J}S(S + 1)/\mathbf{k}$, where $\mathscr{J}$ is the exchange parameter for next-nearest neighbours.[20] For CoO and NiO, $T_{\mathrm{N}} = 292$ and 523 K respectively,[21] and hence $(4/9)\mathscr{J}_{\mathrm{Ni}}/\mathscr{J}_{\mathrm{Co}} = 1{\cdot}49$. However, allowance for the orbital magnetism of CoO reduces this to **1·34**.[6] Note that above the Néel temperature of CoO, spin–orbit coupling makes μ_{eff} decrease with increasing temperature, and hence the correction results in a higher value of $|\mathscr{J}|$, the reverse of the situation we have been considering.

[20] J. S. Smart, 'Effective Field Theories of Magnetism,' Saunders, Philadelphia, 1966.

[21] M. Foëx, *Compt. rend.*, 1948, **227**, 193.

[22] R. K. Nesbet, *Phys. Rev.*, 1960, **119**, 658.

[23] Ref. 19, p. 48.

[24] P. W. Anderson, *Phys. Rev.*, 1959, **115**, 2.

energies of the transitions from $^4T_1(F)$ to $^4T_2$, $^4A_2$, and $^4T_1(P)$, respectively. For compounds (III)—(V) discussed

$$\begin{aligned} 15B &= \tfrac{1}{2}[E_3 - 2E_1 + (E_3^2 + E_1E_3 - E_1^2)^{\frac{1}{2}}] \\ 10Dq &= 2E_1 - E_3 + 15B = E_2 - E_1 \end{aligned} \qquad (8)$$

in this paper, E_1 = 9000—11 000 cm^{-1} and E_2 and E_3 are both in the range 18 000—24 000 cm^{-1}, and we can obtain reasonable fits to the observed spectra with $10Dq$ = 10 000—12 000 and $15B$ = 12 000—14 000 cm^{-1}. By analogy with the nickel complexes [1] we expect similar values in compounds (I), (II), and (VI). Hence $a = 0{\cdot}97 \pm 0{\cdot}01$ and $b = 0{\cdot}25 \pm 0{\cdot}01$, *i.e.* the ground configuration is about 94% $t_2^1e^2$.

The factor A which appears in equation (2) is defined so that the matrix of $\mathbf{L}$ within the ground T_1 term is $-A$ times the matrix within a P term, and it follows that A is equal to $\frac{1}{2}(2a^2 + 4ab - b^2)$. Hence in our compounds $A = 1{\cdot}39 \pm 0{\cdot}02$.

The second-order perturbation of the ground term by the magnetic field contributes a temperature-independent paramagnetic susceptibility given by (9), where the sum is over all m states ψ_{oi} of the ground term and all excited states ψ_{nj}

$$\chi_{\text{tip}} = \frac{2N\mu_B^2}{3m}\frac{|\langle\psi_{nj}|\mathbf{L}|\psi_{oi}\rangle|^2}{E_n - E_o} \qquad (9)$$

such that $E_n - E_o \gg \mathbf{k}T$. Since $\mathbf{L}$ transforms as T_1 in cubic symmetry, both the $^4T_2(F)$ and $^4T_1(P)$ terms will contribute to the t.i.p. of a $^4T_1(F)$ ground term. The contributions in the d^3 or d^7 case are found to be $N\mu_B^2(2k'a + kb)^2/E_1$ from $^4T_2$ and $N\mu_B^2(2k'b^2 + 3kab - 2k'a^2)/3E_3$ from $^4T_1(P)$, where k and k' are orbital reduction factors for $\langle t_2|\mathbf{l}|t_2\rangle$ and $\langle t_2|\mathbf{l}|e\rangle$, respectively. If we assume $k' = k$, we have:

$$\chi_{\text{tip}} = N\mu_B^2k^2(2 + 2A)[1/E_1 + (3 - 2A)/3E_3]$$

The result for d^2 or d^8 is the same. For our compounds only the $^4T_2$ contribution is significant, and $\chi_{\text{tip}} = 0{\cdot}000125k^2$. The average value $k^2 = 0{\cdot}8$ was used in making the t.i.p. corrections.

APPENDIX II

Orbital Exchange Parameters for d⁸–d⁸ *and* d⁷–d⁷ *Interactions.*—The $^3A_2$ ground term of d^8 belongs to the strong-field 'hole' configuration e_g^2, and we may therefore write the exchange matrix in the nickel case as (10), where $\mathscr{H}_{SS}$ is defined by (3) and the abbreviation $|\phi\rangle_{A,B}$ is used for the

$$\langle e^2\,{}^3A_2a_2M_S'|_{A,B}\mathscr{H}_{SS}|e^2\,{}^3A_2a_2M_S\rangle_{A,B} \qquad (10)$$

product $|\phi\rangle_A|\phi\rangle_B$. The orbital and spin functions are separable, and the spin part of (3) can be shown to be equivalent to the operator $-2\mathbf{S}_A\,.\,\mathbf{S}_B/4S^2$ acting on the components of $^3A_2 \times {}^3A_2$. In terms of the real e_g-orbitals, the orbital function is $|e^2A_2a_2\rangle = |\theta\varepsilon\rangle$, and hence (3) reduces to (4).

The $^4T_1(F)$ term of d^7 is a mixture of $t_2^2e^1$ and $t_2^1e^2$ functions, with the latter contributing *ca.* 94% of the electron density in the present case, as noted above. In view of the many other sources of uncertainty in the estimation of the exchange parameters from the data, we make the approximation of neglecting the $t_2^2e^1$ component, and take the ground-state wavefunctions as $|e^2t_2{}^4T_1M_LM_S\rangle$. By partially expanding these determinantal functions, bearing in mind that the only term of e^2 that is a parent of $^4T_1$ is $^3A_2$, we obtain (11), where μ represents one of the real t_2 orbitals ξ, η, and ζ, and the two-electron functions are still antisymmetrised. It can again be shown that the spin part of (3)

$$\begin{aligned} |e^2t_2\,{}^4T_1M_LM_S\rangle = \frac{1}{\sqrt{3}}\sum_{\bar{M}_S}\sum_{m_S}\sum_{\mu} \\ \{|e^2(12)^3A_2a_2\bar{M}_S\rangle|t_2(3)\mu m_S\rangle \\ + |e^2(23)^3A_2a_2\bar{M}_S\rangle|t_2(1)\mu m_S\rangle \\ + |e^2(31)^3A_2a_2\bar{M}_S\rangle|t_2(2)\mu m_S\rangle\} \\ \langle a_2\mu|T_1M_L\rangle\langle\bar{M}_Sm_S|\tfrac{3}{2}M_S\rangle \end{aligned} \qquad (11)$$

is equivalent to the operator $-2\mathbf{S}_A\,.\,\mathbf{S}_B/4S^2$ acting on the components of $^4T_1 \times {}^4T_1$, and the exchange matrix is therefore given by (12), where the operators are defined by (13) and the subscript A,B indicates, as before, the product of the corresponding terms for the A and B ions.

$$\begin{aligned} &\langle{}^4T_1M_L'M_S'|_{A,B}\mathscr{H}_{SS}|{}^4T_1M_LM_S\rangle_{A,B} = \\ &\quad\langle M_S'|_{A,B} - 2\mathbf{S}_A\,.\,\mathbf{S}_B/4S^2|M_S\rangle_{A,B} \\ &\times\sum_{\mu_A}\sum_{\mu_B}\{\langle T_1M_L'|a_2\mu\rangle_{A,B}\langle e^2A_2a_2|_{A,B}J^{(4)}|e^2A_2a_2\rangle_{A,B} \\ &+\sum_{\mu_B'}\langle T_1M_L'|a_2\mu\rangle_A\langle T_1M_L'|a_2\mu'\rangle_B \\ &\times\langle e^2A_2a_2|_A\langle t_2\mu'|_BJ^{(2)}|e^2A_2a_2\rangle_A|t_2\mu\rangle_B \\ &+\text{(a similar term with } A \text{ and } B \text{ interchanged)} \\ &+\sum_{\mu_A'}\sum_{\mu_B'}\langle T_1M'|a_2\mu'\rangle_{A,B}\langle t_2\mu'|_{A,B}J^{(1)}|t_2\mu\rangle_{A,B}\} \\ &\times\langle a_2\mu|T_1M\rangle_{A,B} \end{aligned} \qquad (12)$$

$$\begin{aligned} J^{(1)} &= J(3,3) \\ J^{(2)} &= \sum_{i=1}^{2} J(i,3) \\ J^{(4)} &= \sum_{i=1}^{2}\sum_{j=1}^{2} J(i,j) \end{aligned} \qquad (13)$$

If the matrix of $J^{(1)}$ is diagonal in μ_A and μ_B, (12) becomes diagonal in M_{LA} and M_{LB} and $\mathscr{H}_{SS}$ takes the simple form (5), where $\mathscr{J}(M_{LA},M_{LB})$ is defined by (14) and its non-zero components are given by (15) [equivalent to (6)].

$$\begin{aligned} &\mathscr{J}(M_{LA},M_{LB}) = \tfrac{1}{9}\{\langle e^2A_2a_2|_{A,B}J^{(4)}|e^2A_2a_2\rangle_{A,B} \\ &+\sum_{\mu_A}\langle e^2A_2a_2|_A\langle t_2\mu|_BJ^{(2)}|e^2A_2a_2\rangle_A|t_2\mu\rangle_B|\langle T_1M_L|a_2\mu\rangle|^2{}_B \\ &+\text{(a similar term with } A \text{ and } B \text{ interchanged)} \\ &+\sum_{\mu_A}\sum_{\mu_B}\langle t_2\mu|_{A,B}J^{(1)}|t_2\mu\rangle_{A,B}|\langle T_1M_L|a_2\mu\rangle|^2{}_{A,B}\} \end{aligned} \qquad (14)$$

$$\begin{aligned} \mathscr{J}(\pm1,\pm1) = \mathscr{J}(\pm1,\mp1) &= [J(\theta\theta) + 2J(\theta\varepsilon) + \\ &\quad J(\varepsilon\varepsilon) + 2J(\theta\xi) + 2J(\varepsilon\xi) + \tfrac{1}{2}J(\xi\xi) \\ &\quad + \tfrac{1}{2}J(\xi\eta)]/9 \\ \mathscr{J}(\pm1,0) = \mathscr{J}(0,\pm1) &= [J(\theta\theta) + 2J(\theta\varepsilon) + J(\varepsilon\varepsilon) + \\ &\quad J(\theta\zeta) + J(\varepsilon\zeta) + J(\theta\xi) + J(\varepsilon\xi) + \\ &\quad J(\xi\zeta)/9 \\ \mathscr{J}(0,0) &= [J(\theta\theta) + 2J(\theta\varepsilon) + J(\varepsilon\varepsilon) + 2J(\theta\zeta) + \\ &\quad 2J(\varepsilon\zeta) + J(\zeta\zeta)]/9 \end{aligned} \qquad (15)$$

APPENDIX III

Susceptibility of a Pair of Ions in T₁ *or* T₂ *Orbital States.*—The magnetic behaviour of a pair of $^4T_{1g}$ ions perturbed by the Hamiltonian (2) with the exchange operator defined by (5) was calculated by means of two computer programs. Program TTMAG1 prepares a magnetic tape containing the necessary vector-coupling coefficients and the matrices of $\mathscr{H}_{LL}$, $\mathscr{H}_{LS}$, and $\mathscr{H}_{SS}$ with parameters omitted. Program

TTMAG2 is supplied with this tape and one or more sets of the parameters λ, D, *etc.*, and calculates the susceptibility–temperature curves. These programs can also deal with $^2T_2$ and $^3T_1$ ions. They are written in Fortran and require (for $^4T_1$) core storage for at least 40 000 real numbers, or 16 000 if disc backing store is used. A program is also available for the case of two $^2T_2$, $^3T_1$, $^4T_1$, or $^5T_2$ ions in effectively cubic environments with isotropic exchange.

Testing of the Computer Programs.—The correctness of the programs was checked as follows (assuming isotropic exchange).

(i) With $D = \mathscr{J} = 0$ and $S = \frac{1}{2}, 1, \frac{3}{2}$, and 2, the programs gave results identical with those calculated for isolated $^2T_2$, $^3T_1$, $^4T_1$, and $^5T_2$ ions respectively.[10] (ii) With $D = k = 0$ and $S = \frac{1}{2}, 1, \frac{3}{2}$, and 2, they gave results identical with those calculated for a pair of exchange-coupled spin-only ions with $g = 2$.[25] (iii) With $\mathscr{J} = 0$ and $S = \frac{1}{2}$ they gave results that agreed with those calculated for isolated $^2T_2$ ions with an axial distortion.[26] (iv) With $\mathscr{J} \neq 0$, as $D \longrightarrow \pm\infty$ the results approached those calculated for a pair of exchange-coupled spin-only ions. (v) With $D = 0$ and $S = \frac{1}{2}$, the calculated curves of μ_{eff} against $\mathbf{k}T/\lambda$ for various $\mathscr{J}/\lambda$ agreed with those of Kahn.[9a]

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