

Binuclear Cobalt(II) and Nickel(II) Complexes of Dihydrazinophthalazine and Dipyridylpyridazine: the Dependence of Superexchange on Electronic Configuration

By J. E. ANDREW, P. W. BALL, and A. B. BLAKE*

(Department of Chemistry, University of Hull)

ONE method of investigating possible superexchange mechanisms, which has been widely applied to lattice anti-ferromagnets,¹ is to measure the strength of the exchange interaction on the electronic configurations of the magnetic ions when the diamagnetic environment is constant. Among polynuclear complexes such direct comparisons have been possible in only a few cases, e.g. $[M(OAc)_2]_2$ ($M = Cr^{II}$ or Cu^{II}),² $[M_3O(OAc)_6(H_2O)_3]Cl$ ($M = Cr^{III}$ or Fe^{III}),³ and $[Msal(OMe)(EtOH)]_4$ ($M = Co^{II}$ or Ni^{II}),⁴ but we have investigated the properties of several ligands which tend to form binuclear complexes. We now report the results of a magnetic and structural study of some cobalt(II) and nickel(II) complexes of 1,4-dihydrazinophthalazine [dhph (I)], 3,6-di-(2-pyridyl)pyridazine [dppn (II)], and 3,6-di-(6-methyl-2-pyridyl)pyridazine [Me_2dppn (III)], which has made possible a comparison of the superexchange behaviour of these two metals in similar environments.

Complexes of (I) were prepared by mixing aqueous solutions of NiX_2 or CoX_2 and dhph, HX ($X = Cl, Br, \text{ or } I$). Complexes of (II) and (III) were prepared from the ligand and the appropriate metal salt in water (perchlorates), aqueous ethanol (sulphates), or methanol-triethyl orthoformate (nitrates). Satisfactory analytical results were obtained in all cases.

Magnetic parameters for binuclear cobalt(II) and nickel(II) complexes

Compound	M = Co		M = Ni		J_{Ni}/J_{Co}
	g	$-J/k$	g	$-J/k$	
M dhph $Cl_2 \cdot nH_2O^a$	2.39	10.6°	2.15	32.1°	3.0
M dhph $Br_2 \cdot 3H_2O$	2.41	11.9	2.16	34.3	2.9
M dppn $(NO_3)_2 \cdot H_2O$	2.38	10.6	2.22	33.8	3.2
M dppn $(ClO_4)_2 \cdot nH_2O^b$	2.26	8.2	2.15	21.1	2.6
M_2 dppn $(SO_4)_2 \cdot 5H_2O$	2.41	7.5	2.18	17.7	2.4
M_2 Me_2dppn $(NO_3)_4 \cdot 2ROH^c$	2.41	11.6	2.18	29.8	2.6
M Me_2dppn $(ClO_4)_2 \cdot nH_2O^{b,d}$	2.41	2.2	2.18	4.0	

^a M = Co, $n = 2.5$; M = Ni, $n = 3$.

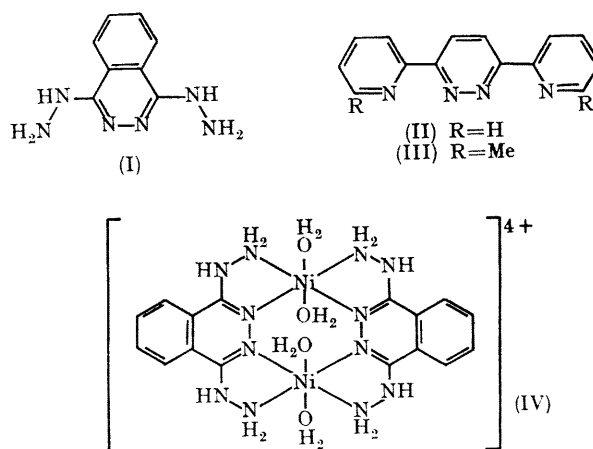
^b M = Co, $n = 3$; M = Ni, $n = 2$.

^c M = Co, R = Me; M = Ni, R = H.

^d Probably mononuclear.

The crystal structure of Ni dhph $Cl_2 \cdot 3H_2O$ has been determined by single-crystal X-ray methods and refined by least-squares ($R = 0.14$).⁵ The triclinic unit-cell contains a single centrosymmetric binuclear cation $[Ni_2 dhph_2(H_2O)_4]^{4+}$, (IV), in which each dhph molecule is chelated to both nickel ions in a *trans*-planar arrangement, with approximately octahedral co-ordination completed by four water molecules. The Ni-Ni distance of 3.79 Å precludes significant direct overlap of nickel orbitals, so that any interaction must be through the N-N bridges. The presence of an exchange interaction is indicated by the decrease in the magnetic moment per nickel ion from 2.83 B.M. at 300° to 2.11 B.M. at 80° K. The cobalt complexes of (I) are not isomorphous with their nickel analogues, but their i.r. spectra are so similar that they must have essentially the same structure.

The evidence for the structures of the complexes of (II) and (III) is indirect. The nickel complexes with metal:ligand ratios of 1:1 and 2:1 all have magnetic moments that decrease from ca. 2.9 B.M. at 300° to ca. 2.3 B.M. at 80° K, suggesting binuclear structures, whereas $NiMe_2dppn_2(ClO_4)_2 \cdot 2H_2O$ shows normal paramagnetic behaviour and is presumably mononuclear. The electronic spectra of the 1:1 nickel complexes show four bands, at ca. 10,000, 12,000, 17,000, and 18,000 cm^{-1} , which we interpret as the components of the octahedral ν_1 and ν_2 transitions split by a moderate tetragonal distortion of the crystal field. The



complexes with metal:ligand ratios of 2:1 or 1:2, on the other hand, show only two broad bands, indicating a considerably smaller deviation of the field from cubic symmetry. Since the arrangement of ligand atoms in the latter types is almost certainly *cis*- N_2O_4 and *cis*- N_4O_2 respectively, we conclude that the arrangement in the 1:1 complexes is *trans*- N_4O_2 . A binuclear structure with bridging chelate dppn molecules, analogous to (IV), is the only reasonable one consistent with these facts. A singly bridged binuclear structure is assigned to the 2:1 complexes. With M dppn- $(NO_3)_2 \cdot H_2O$ and M $Me_2dppn_2(ClO_4)_2 \cdot nH_2O$ the cobalt and nickel complexes are isomorphous, while in the other cases similarity of structure is indicated by the i.r. spectra.

For both the nickel and cobalt complexes an exchange interaction of the form $-2JS_1 \cdot S_2$ was assumed, and the corresponding expression for the susceptibility⁶ was fitted to the experimental data to give the values of the g -factor and the exchange parameter J listed in the Table. The fit was in all cases within the estimated experimental error.

Allowing for an uncertainty of $\pm 5\%$ in J (arising mainly from packing of the powders), the values for the nickel and cobalt complexes show a reasonably constant ratio of ca. 2.8:1. According to the theories of Anderson⁷ and Nesbet,⁸ if the exchange interaction takes place through a σ -bond pathway, so that only one e_g orbital of each ion contributes,

and if the efficiency of the exchange process is the same for cobalt and nickel, then J should vary inversely as the square of the number of unpaired electrons, *i.e.* $J_{Ni}/J_{Co} = 2.25$. The observed ratio of 2.8 suggests that exchange is somewhat more efficient in the case of nickel, possibly because of ferromagnetic terms arising from the t_{2g} spin of the Co^{2+} ions.

It should be pointed out that the above procedure for the estimation of J is not strictly applicable to octahedral cobalt(II) complexes, since it ignores the effect of spin-orbit coupling within the ${}^4T_{1g}$ ground term. We have recently

calculated the magnetic behaviour of a pair of exchange-coupled ions with cubic-field T -type ground terms, as a function of the spin-orbit coupling, exchange, and ligand-field parameters.⁹ The calculations are not well adapted to curve-fitting procedures, but initial results indicate that the spin-only approach used above may overestimate the value of J_{Co} by as much as a factor of 2. This would suggest a substantial ferromagnetic contribution to the net interaction in the cobalt case.

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