Five-co-ordinate, Binuclear Nickel(II) Complexes

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Summary Magnetic susceptibility measurements indicate interaction between nickel atoms with $S = 1$ in some binuclear nickel(II) orthoquinoneoxime complexes.

ALTHOUGH there are numerous examples of binuclear copper(II) complexes the number of corresponding nickel(II) complexes is comparatively small.[1] Furthermore, the binuclear nickel(II) compounds so far reported appear to be six-co-ordinate. We have prepared a number of binuclear five-co-ordinate complexes of formula $[Ni(QO)_2]_2$ (QOH is 4-chloro-2-nitrosophenol, 4-bromo-2-nitrosophenol, 4-methyl-2-nitrosophenol or 4-t-butyl-2-nitrosophenol).

The complexes, which had satisfactory analyses, were prepared by methods previously described.[2] The room temperature magnetic moments are anomalous[3] (Table) and are *ca.* 0·2 B.M. less than the room temperature moments of other binuclear nickel(II) complexes.[1,4] The susceptibility over a temperature range follows that expected for two interacting metal atoms each having $S = 1$.[5]

TABLE

Magnetic data

	μ_{eff}(B.M.)	g	$-J$ cm.$^{-1}$
$Ni(4\text{-}ClQO)_2$	2·53	2·07	38
$Ni(4\text{-}BrQO)_2$	2·67	2·19	41
$Ni(4\text{-}MeQO)_2$	2·70	2·23	41
$Ni(4\text{-}Bu^tQO)_2$	2·64	2·14	34

The mass spectra of the compounds have peaks with *m/e* greater than the monomer and the isotopic splitting patterns indicate that at least some of the peaks have two nickel atoms.

The molecular weights in chloroform of the chloro- and t-butyl-complexes (the other two complexes were insoluble) are 740 and 820, respectively, which correspond closely to twice the formula weight in each case.

The most likely structure of the dimers involves bonding between an oxygen atom of one $Ni(QO)_2$ species and the nickel atom of the other so that both nickel atoms are five-co-ordinate. The complexes react with pyridine (py) to give adducts of composition $Ni(QO)_2,2py$. The adducts have "normal" room temperature moments (*ca.* 3·1 B.M.) and electronic spectra typical of octahedrally co-ordinated nickel(II), but the electronic spectra of the dimers are quite different.

The structure suggested for the $[Ni(QO)_2]_2$ compounds is fairly common in copper chemistry *e.g.* bis(dimethylglyoximato)copper(II)[6] and β-bis-(8-quinolinolato)copper(II),[7] but in these cases there is no magnetic interaction between adjacent copper atoms.[8] In a d^9 system it is difficult to construct a π-system involving the unpaired electron in a metal d_{z^2} orbital but in the square pyramidal high spin d^8 system it is possible that the $d_{x^2-y^2}$ orbital of one nickel atom could form a π-system with the p_y orbital of the ligand oxygen atom and the d_{yz} orbital of the other nickel atom.

(*Received, July 4th,* 1969; *Com.* 975.)

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