

μ -Phenazine-5,10-dioxidetetrnickel(II) Chloride Tetrahydrate

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During recent studies of phenazine 5,10-dioxide (L) complexes with 3d metal salts,¹ an unusual 1:4 complex of L with NiCl₂, analyzing as (NiCl₂)₄L·4H₂O (analysis by Schwarzkopf, Woodside, N.Y.: Found (Calc.)%: C 17.53(17.95); H 2.12(2.21); N 3.53(3.49); Ni28.90(29.30)), was prepared at these laboratories.² The complex was isolated by refluxing overnight a suspension of NiCl₂ in a chloroform solution of L, and subsequently filtering the hygroscopic maroon precipitate (in a dry-box; N₂ atmosphere), washing with hexane and storing in an evacuated desiccator over P₂O₅. L was prepared by the method of Clemo and McIlwain.³

The solid-state (Nujol mull) electronic spectrum of the new complex favors a pseudo-tetrahedral symmetry,^{4,5} viz. (nm): ligand bands^{6,7} at 230s, 256sh, 273sh, 290vs, 466w, 475m, 488w, 497m, 507m; (*d-d*) transitions: ³T₁(F) → ¹G 548m; → ³T₁(P) 696m, sh, 760m-2, sh; → ¹E, ¹T₂(D) 910w, sh; → ³A₂(F) 1340w,sh; → ³T₂(F) 1953m-w(sharp). The infrared spectrum of L at 1400-1000 cm⁻¹ is as follows (cm⁻¹): 1385w,sh, 1366m,sh, 1346s, 1270m, 1257m,sh, 1206m, 1172w, 1145w, sh, 1111w, 1085s, 1008m. The bands at 1270, 1257 cm⁻¹ are associated with the ν_{N-O} mode,⁸ while the strong absorption at 1085 cm⁻¹ is presumably due to a CNO mode with considerable C-N stretching character (*i.e.*, $\nu_{C-N(O)}$), as established for the corresponding acridine N-oxide band,⁹ which is invariably shifted to lower wavenumbers upon metal complex formation.¹⁰ The new complex shows the following ir spectrum in the same region (cm⁻¹): 1394w, 1338s, 1291w,sh, 1282m, 1249w,sh, 1229w, 1174m, 1125w, 1079s, 1074s, 1029m. The ν_{N-O} region of this spectrum is rather complicated to allow conclusions regarding the direction of the ν_{N-O} shift (most probably owing to considerable overlaps between ν_{N-O} and aromatic ring vibrations in the spectrum of free L^{10,11}). However, in the $\nu_{C-N(O)}$ region, the complex clearly shows a negative frequency shift (doublet at 1079, 1074 cm⁻¹), relative to the position of this band in free L; this evidence favors coordination of L through both its oxygens, *i.e.*, as a bridging, bidentate ligand.^{10,12,13} Tentative

metal-ligand band assignments ($\nu_{Ni-O(L)}$ 415,396;¹⁴ ν_{Ni-Cl} 342,326;¹⁵ $\nu_{Ni-O(aquo)}$ 497,490¹⁶ cm⁻¹) favor coordination number four for each Ni²⁺ ion.¹⁴⁻¹⁶ The presence of coordinated water is also indicated by the occurrence of ν_{OH} as a strong, broad band at 3385 cm⁻¹.¹⁶ The overall evidence rules out the possibility that part of the nickel present is in the form of the tetrachloronickelate(II) anion, which shows the ν_{Ni-Cl} mode at 289 cm⁻¹,¹⁵ and a *d-d* transition spectrum,⁴ distinctly different from that observed for the new complex.

The magnetic properties of the new complex are interesting and favor a polynuclear structure. In fact, the μ_{eff} values of monomeric tetrahedral Ni(II) compounds decrease with decreasing temperature.¹⁷ In contrast, the χ values of the new complex increase with decreasing temperature in the 80-297 °K region, while its magnetic moment shows an increase from 3.43 μ_B at 297 °K to 3.58 μ_B at 100 °K, and then sharply decreases to 3.42 μ_B at 80 °K (Table I).

TABLE I. Magnetic Properties of (NiCl₂)₄L·4H₂O.

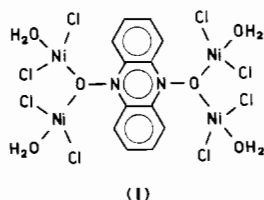
Temperature, °K	10 ⁶ χ_A^{COR} , cgsu ^a	μ_{eff} , B
80.8	17,902	3.42
100.0	15,855	3.58
117.2	13,191	3.53
134.5	11,283	3.50
152.1	9,861	3.48
169.6	8,784	3.47
187.8	7,891	3.46
205.1	7,203	3.45
223.4	6,600	3.45
242.0	6,073	3.44
260.4	5,622	3.43
279.3	5,257	3.44
297.6	4,914	3.43

^a χ_A is the magnetic susceptibility per Ni atom of the tetranuclear complex.

Similar magnetic behavior has been reported for the trimeric, linear bis(acetylacetonato)Ni(II)¹⁸ and a number of bi- or tri-nuclear Ni(II) complexes with Schiff bases,¹⁹ and attributed to the combined effects of ferromagnetic interactions between adjacent Ni atoms and antiferromagnetic intra- (between extreme Ni atoms in trimeric linear complexes) or inter- (in binuclear complexes) molecular interactions.^{18,19} It should be noted that in these complexes the sharp decrease of μ_{eff} occurs at very low temperatures (4-5 °K), immediately after a maximum of 4.0-4.1 μ_B has been reached.^{18,19} It is possible that in the new Ni(II) complex, in addition to the above effects, spin-spin coupling by magnetic superexchange between oxygen-bridged (Ni-O-Ni bridges)

Ni atoms, becomes important at low temperatures. Even at room temperature, the μ_{eff} of the complex (3.43 μB) is somewhat low for tetrahedral Ni(II).^{17,20} Magnetic superexchange of the above type is quite common in binuclear O-bridged Cu(II) complexes with various ligands, including aromatic amine N-oxides.^{13,21}

A probable structure for $(\text{NiCl}_2)_4\text{L}\cdot 4\text{H}_2\text{O}$, consistent with the overall evidence presented, is I.



This tetranuclear structure involves a L molecule, each oxygen site of which functions as a bridge between two Ni^{2+} ions. It is hoped that, in the near future, the facilities available to us will allow the extension of the magnetic susceptibility studies of the complex to temperatures below 80 °K, in order to improve the understanding of the magnetic behavior of this compound.

Spectral measurements were obtained by methods previously described.²² Magnetic susceptibility studies were performed by Professor A. B. P. Lever's laboratory (York University, Toronto, Ont., Canada). Studies of the complex in solution (conductance, electronic spectrum, etc.) were precluded by its instability in suitable organic solvents (e.g., nitromethane, dimethyl sulfoxide, N,N-dimethylformamide). In fact, upon dissolution of the complex in organic polar solvents, the resulting reddish solution changes rapidly to orange, which is the color of free L, and indicative of dissociation of the complex.

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