Magneto-Structural Correlations in Phenoxo-Bridged Metal(II) Compounds. Magnetic Properties of $(R_4N)_2[Co_2Cl_4(4\text{-}XC_6H_4O)_2]$ ($X = H, CH_3$; $R = CH_3, C_2H_5$)

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(Received April 16, 1999)

Dinuclear compounds $(R_4N)_2[Co_2Cl_4(4\text{-}XC_6H_4O)_2]$ (X = H, CH_3; R = CH_3, C_2H_5) were prepared, and their temperature-variable magnetic susceptibilities were determined to evaluate the exchange-coupling strength's between the cobalt(II) ions. The coupling strength of $(Et_4N)_2[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$ was considered in terms of its structural parameters and the electronic effects of the methyl substituent. Such magneto-structural correlations, together with those for copper(II), nickel(II), and iron(II) systems, confirm that the exchange couplings in phenoxo-bridged metal(II) compounds are affected concurrently by the *s*/*p* character of the hybrid orbitals on the bridging oxygen atom, by the electronic effects of the substituents on the aromatic ring, by the ionic radius and acidity of the metal(II) ion, as well as by the number of unpaired electrons and *d* character of the hybrid orbitals on the metal(II) ion.

A number of experimental and theoretical investigations have been carried out concerning the structures and magnetic properties of phenoxo-bridged transition-metal compounds.[1—15] Particular interest has been focused on the different magnetic behaviors among the unsubstituted and various substituted phenoxides. During these studies, it was found that the exchange-coupling strength in a phenoxo-bridged metal(II) compound can be inferred in terms of both the bridging geometry and the electronic effects of the substituents on the aromatic ring.[3]

In the meantime, Pilkington and Robson in 1970 were intrigued about the preparation and characterization of a series of compounds, M_2LCl_2 (M = Cu, Ni, Fe, Mn), with a macrocyclic dinucleating ligand, H_2L.[4] For these phenoxides, Lambert and Hendrickson attempted to explain the exchange-coupling strength's by considering the number of unpaired electrons, the ionic radii of metal(II) ions, and the associated exchange pathways.[6] In order to understand such coupling variations, however, the difference in the bridging geometrys should be taken into account, because substitution of the metal(II) ion may change the structural parameters. At present, magneto-structural correlations for phenoxides with metal(II) other than copper(II) and nickel(II) ions, especially those with cobalt(II) ion, are unclear owing to rare reliable magnetic data for structurally characterized compounds.

Recently, Coucouvanis et al. prepared a series of compounds, $(Et_4N)_2[M_2(4\text{-}CH_3C_6H_4O)_2Cl_4]$ (M = Zn, Co, Fe, Mn), in order to compare the structures and substitution reactions.[10] These compounds are well suited for evaluations of the exchange-coupling strength in dinuclear compounds with tetrahedral coordinated metal(II) ions to investigate multi-variable magneto-structural correlations for the phenoxo-bridged cobalt(II) system. We thus examined the magnetic behaviors of $(Et_4N)_2[Co_2(4\text{-}CH_3C_6H_4O)_2Cl_4]$ and its related compounds. We redetermined the crystal structure of $(Et_4N)_2[Co_2(4\text{-}CH_3PhO)_2Cl_4]$ to obtain structural parameters of the crystals used for the magnetic studies.

Experimental

Compounds of the type $(R_4N)_2[Co_2Cl_4(4\text{-}XC_6H_4O)_2]$ (X = H, CH_3; R = CH_3, C_2H_5) were prepared according to the reported procedures.[10] Anhydrous cobalt(II) chloride was allowed to react with equimolar tetraalkylammonium chloride and sodium phenoxide in refluxing acetonitrile under a dry atmosphere (dried over silica gel) for 6 h. Large blue crystals slowly grown from the solutions were collected: $(Me_4N)_2[Co_2Cl_4(C_6H_5O)_2]$ (**1**), $(Me_4N)_2[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$ (**2**), $(Et_4N)_2[Co_2Cl_4(C_6H_5O)_2]$ (**3**), and $(Et_4N)_2[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$ (**4**). Found for **1**: Co, 19.84; C, 40.4; H, 5.76; N, 4.71%. Calcd for $CoC_{10}H_{17}NOCl_2$: Co, 19.84; C, 40.4; H, 5.77; N, 4.71%. Found for **2**: Co, 18.94; C, 42.4; H, 6.14; N, 4.52%. Calcd for $CoC_{11}H_{19}NOCl_2$: Co, 18.94; C, 42.5; H, 6.16; N, 4.50%. Found for **3**: Co, 16.68; C, 47.8; H, 7.12; N, 3.99%. Calcd for $CoC_{14}H_{25}NOCl_2$: Co, 16.69; C, 47.6; H, 7.13; N, 3.97%. Found for **4**: Co, 16.08; C, 49.2; H, 7.40; N, 3.82%. Calcd for $CoC_{15}H_{27}NOCl_2$: Co, 16.05; C, 49.1; H, 7.41; N, 3.81%.

The magnetic susceptibilities of compounds **1**—**4** were determined over the temperature range 2.0—300 K, and corrected for diamagnetic contributions using Pascal constants,[16] and for temperature-independent paramagnetism using a value of 6.3×10^{-9} $m^3\,mol^{-1}$ for the cobalt(II) ion. The infrared spectra of the compounds were recorded on a Hitachi 260-10 IR Spectrophotometer in the 4000—650 cm^{-1} range using Nujol® mulls.

The crystal structure of compound **4** was determined by the X-ray diffraction method using a Rigaku AFC-5S diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Intensity data were recorded using $\omega/2\theta$ scans at a scanning rate of 16 deg min^{-1}, and the ratio of the peak counting time to background counting time was 2 : 1. The intensities of three standard reflections were checked every 150 recordings. An empirical absorption correction, based on the average of the azimuthal scans of three reflections, was applied. The range of the correction on the transmission factors was 0.88 to 1.0.

The structure was solved by the direct method and refined by full-matrix least-squares iterations.[17] The dimeric anion had a crystallographic inversion center, which renders the $CoCl_2(OAr)$ unit unique. Thus, a monomeric unit was uniquely determined. All non-hydrogen atoms were readily located without any disorder problems (Table 1). They were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å), and were included in the refinement with isotropic thermal parameters. The final values of the discrepancy indices, R and R_w, were 0.037 and 0.041, for 2529 observed reflections ($> 3\,\sigma$) on 181 variables. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. The standard deviation of an observation of unit weight was 1.26. All of the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Crystal data. $(Et_4N)_2[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$, FW = 367.2, space group $P2_1/n$ (monoclinic), $a = 11.546(1)$, $b = 10.948(3)$, $c = 14.520(1)$ Å, $\beta = 92.840(7)°$, $Z = 4$, $D_c = 1.331$ g cm^{-3}. The unit-cell parameters are similar to those of Coucouvanis et al.[10] A perspective view of the centrosymmetric $[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$ anion is shown in Fig. 1; the anion can be described in terms of two edge-sharing tetrahedral units with each of the cobalt(II) ions coordinated by two terminal chloro and two bridging 4-methylphenoxo ligands. The bond lengths and angles in the anion are given in Table 2. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC-136362.

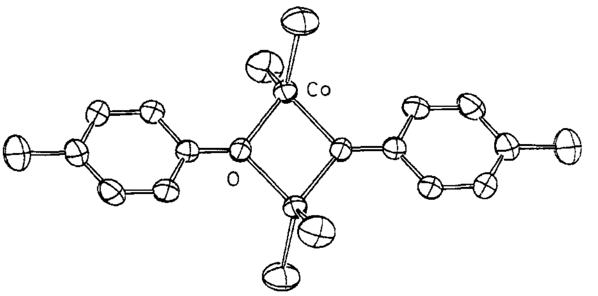

Fig. 1. ORTEP drawing of the $[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$ anion.

Table 1. Positional Parameters for $(Et_4N)_2[Co_2Cl_4(4\text{-}CH_3C_6H_4O)_2]$

Atom	x	y	z
Co(1)	0.43441(4)	0.07136(4)	0.07012(3)
Cl(1)	0.24921(8)	0.1273(1)	0.04970(7)
Cl(2)	0.5154(1)	0.1294(1)	0.20613(7)
O(1)	0.5308(2)	0.0998(2)	−0.0369(1)
N(1)	0.3676(2)	0.2248(3)	0.6160(2)
C(1)	0.5636(3)	0.2039(3)	−0.0772(2)
C(2)	0.5086(3)	0.3142(3)	−0.0594(2)
C(3)	0.5440(3)	0.4224(3)	−0.1007(2)
C(4)	0.6345(3)	0.4224(4)	−0.1596(2)
C(5)	0.6867(3)	0.3117(4)	−0.1785(2)
C(6)	0.6529(3)	0.2050(3)	−0.1374(2)
C(7)	0.6737(5)	0.5399(4)	−0.2019(3)
C(8)	0.3243(4)	0.3546(4)	0.6063(3)
C(9)	0.4101(5)	0.4509(5)	0.6397(4)
C(10)	0.2726(3)	0.1434(4)	0.5748(3)
C(11)	0.2993(5)	0.0086(5)	0.5765(4)
C(12)	0.3950(4)	0.1925(4)	0.7163(3)
C(13)	0.2942(5)	0.1982(6)	0.7761(3)
C(14)	0.4788(3)	0.2085(4)	0.5669(3)
C(15)	0.4695(4)	0.2373(5)	0.4645(3)

Results and Discussion

The IR spectra of the obtained phenoxides showed sharp bands at ca. 1250—1280 cm^{-1} assignable to C–O stretching of the phenoxo groups.[18] The temperature dependence of the magnetic susceptibilities for compounds **1**—**4** exhibited Curie–Weiss behaviors over the range of 70—300 K (g = 2.42 to 2.58 and $\Theta = -0.2$ to -1.8 K); the obtained Weiss constants indicate the existence of small antiferromagnetic interactions among the cobalt(II) ions. The susceptibilities of **1**—**4** over the temperature range 2.0—30 K were simulated using a modified Van Vleck equation for a pair of exchange-coupled $S = 3/2$ spins (Fig. 2),[19]

$$\chi=[Ng^2\beta^2/k(T-\theta)]\times[(14+5x^6+x^{10})/(7+5x^6+3x^{10}+x^{12})]+N\alpha, \tag{1}$$

where $x = \exp(-J/kT)$. The observed and calculated susceptibilities agree well in this temperature range, using constant

Table 2. Intramolecular Distances (Å) and Intramolecular Bond Angles (°)

Atoms	Distance	Atoms	Distance
Co1–Cl1	2.229(1)	C1–C6	1.385(4)
Co1–Cl2	2.235(1)	C2–C3	1.378(4)
Co1–O1	1.980(2)	C3–C4	1.384(5)
Co1–O1	1.981(2)	C4–C5	1.386(5)
O1–C1	1.343(3)	C5–C6	1.377(5)
C1–C2	1.395(4)	C8–C9	1.510(7)
C4–C7	1.505(5)		
Atoms	Angle	Atoms	Angle
Cl1–Co1–Cl2	113.28(4)	O1–C1–C2	120.9(3)
Cl1–Co1–O1	115.17(7)	O1–C1–C6	121.2(3)
Cl1–Co1–O1	115.61(7)	C2–C1–C6	117.9(3)
Cl2–Co1–O1	114.96(7)	C1–C2–C3	120.1(3)
Cl2–Co1–O1	113.80(7)	C2–C3–C4	122.1(3)
O1–Co1–O1	80.13(9)	C3–C4–C5	117.2(3)
Co1–O1–Co1	99.87(9)	C3–C4–C7	121.2(4)
Co1–O1–C1	131.0(2)	C5–C4–C7	121.6(3)
Co1–O1–C1	129.1(2)	C4–C5–C6	121.3(3)
C1–C6–C5	121.2(3)		

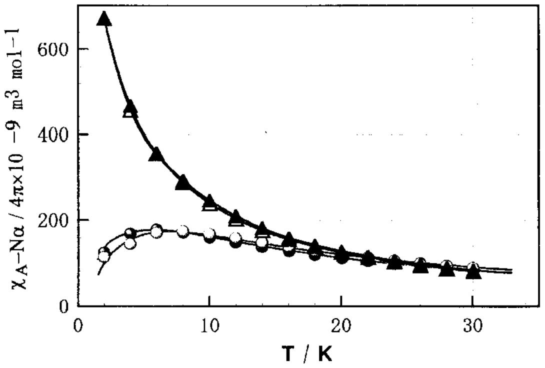

Fig. 2. Temperature dependence of the magnetic susceptibilities for compounds (**1**)—(**4**). The solid curves represent the modified Van Vleck equation.

g values, in agreement with the $^4A_2$ state being the lowest. The obtained parameters are $J = -1.3$ cm^{-1}, $\theta = 0$ K, and $g = 2.48$ for **1**, $J = -0.3$ cm^{-1}, $\theta = 0$ K, and $g = 2.35$ for **2**, $J = -0.2$ cm^{-1}, $\theta = 0$ K, and $g = 2.41$ for **3**, and $J = -1.2$ cm^{-1}, $\theta = -1.5$ K, and $g = 2.63$ for **4**. The susceptibilities of **4** exhibit small interdimer interactions ($\theta = -1.5$ K).

We have previously shown that the exchange-coupling strengths in phenoxo-bridged copper(II) and nickel(II) compounds can be inferred in terms of both the bridging geometry and the electronic effects of the substituents on the aromatic ring. The coupling strengths (J in cm^{-1}) for the copper(II) compounds were formulated using parameters for the geometry (R, ψ, θ, ϕ, τ) and electronic effects (pK_a, pK_π), as follows:[3]

$$J = 100(R/2.00)^{-12}\cos^2\tau\{1 - 1.42(\mathrm{p}K_\mathrm{a} - 20.6\mathrm{p}K_\pi + 154) \times \cos^2\psi[\cos^4\theta/(1 - 0.7\sin^2\theta)^2]\sin^2(30 - \phi)\}, \quad (2)$$

where R (in Å) is the coordination bond length of the phenoxo ligand; ψ, θ, ϕ are the three geometrical parameters around the bridging oxygen atom (i.e., the bridging angle, the dihedral angle, and the azimuthal angle shown in Fig. 3); and τ is the dihedral angle between the CuO_2 plane and the remaining coordinating plane. pK_a is the acidity of the conjugate acid of the phenoxo ligand and pK_π is a correction term for the resonance effect by a substituent on the aromatic ring (pK_a = 10.00, 10.14, 9.98, 9.96, and 10.28; pK_π = −6.77, −7.07, −6.00, −5.23, and −7.38 for hydrogen and 4-alkyl, 2-imino, 2,2′-diimino and 2-alkyl substituents, respectively). The pK_π values were deduced from the resonance and field constants of Swain and Lupton.[20,21]

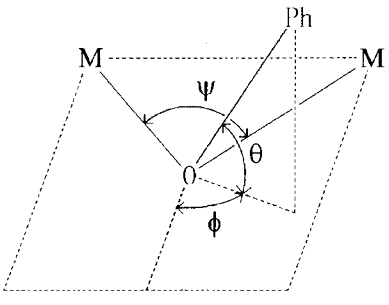

Fig. 3. Coordinate systems for phenoxo bridges.

A similar correlation for nickel(II) compounds is

$$J \times 5.9 = 100(R/2.00)^{-12}\cos^2\tau\{1 - 1.42(\mathrm{p}K_\mathrm{a} - 20.6\mathrm{p}K_\pi + 154) \times \cos^2\psi[\cos^4\theta/(1 - 0.7\sin^2\theta)^2]\sin^2(30 - \phi)\}. \quad (3)$$

Apparently, these facts suggest that the correlations for the compounds with metal(II) ions that have a half-filled d hybrid-orbital directed toward the bridging atom[22,23] are generally

$$J \times AS^2 = (R/2.00)^{-12}\cos^2\tau\{1 - 1.42(\mathrm{p}K_\mathrm{a} - 20.6\mathrm{p}K_\pi + 154) \times \cos^2\psi[\cos^4\theta/(1 - 0.7\sin^2\theta)^2]\sin^2(30 - \phi)\}, \quad (4)$$

where the coefficient AS^2 is 1.00 for copper(II) derivatives and 5.9 for nickel(II) derivatives.

In order to demonstrate the bridging-angle dependence of Eq. 4 graphically by fixing the remaining parameters as $\theta = 0°$, $\phi = 0°$, $\tau = 0°$, $R = 2.00$ Å, pK_a = 10.00, and pK_π = −6.77, we plotted the J^{corr} values for the copper(II) and cobalt(II) compounds against the bridging angles in Fig. 4, where

$$J^{\mathrm{corr}} = 6.43 \times [J(R/2.00)^{12}/\cos^2\tau - 100]/ (\mathrm{p}K_\mathrm{a} - 20.6\mathrm{p}K_\pi + 154)[\cos^4\theta/(1 - 0.7\sin^2\theta)^2] \times \sin^2(30 - \phi) + 100. \quad (5)$$

An X-ray crystal structure analysis of compound **4** shows that $R = 1.980$ Å, $\psi = 99.87°$, $\theta = 0.13°$, $\phi = 1.0°$, $\tau = 71.0°$, allowing us to calculate the J^{corr} value for **4**. Figure 4 indicates that Eq. 4 is consistent with the exchange constants for the cobalt(II) compounds[5,10] if AS^2 is assumed to be 16.4. Hence, it has been confirmed that the primary factor influencing the exchange couplings for the phenoxo-bridged cobalt(II) system is also the s/p character of hybrid orbitals on the bridging oxygen atom (Goodenough–Kanamori rule).[22,23]

It is natural to assume that the acidity of metal(II) ions affects the strengths of the exchange coupling, since the basicity of bridging ligands affects the strengths of the exchange coupling (pK_a term). We then have attempted to correlate the above-mentioned variation in the exchange couplings for

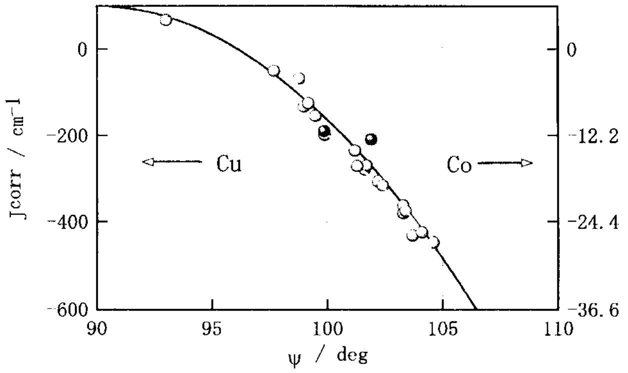

Fig. 4. Bridging-angle dependence of the exchange couplings for phenoxo-bridged copper(II) compounds (○) and cobalt(II) compounds (●). The solid curve represents Eq. 4 in the text.

the series of copper(II), nickel(II), and cobalt(II) compounds with the ionization energies of metal(II) ions (the Usanovich acid-base concept);[24] the correlations can be summarized as

$$\begin{aligned} J \times 4S^2 = 23000 \times (IE/100)^{3.4}(R/2.00)^{-12}\cos^2\tau \\ \times\{1 - 1.42(\mathrm{p}K_\mathrm{a} - 20.6\mathrm{p}K_\pi + 154)\cos^2\psi \\ \times[\cos^4\theta/(1-0.7\sin^2\theta)^2]\sin^2(30-\phi)\}, \end{aligned} \tag{6}$$

where IE is the ionization energy (IE = 20.3, 18.2, 17.1 eV, for copper(II), nickel(II), and cobalt(II) ions, respectively).[24] This situation arises from the mixing of small amounts of excited states into the ground state; a partial transfer of the electron spin density from a ligand orbital into a half-filled *d* orbital on one of the metal(II) ions yields an excited state. By substituting 2 for S and 16.2 eV for IE in Eq. 6, we can anticipate the coupling strengths for iron(II) compounds which agree well with the experimentally determined strengths (for example, $J = -0.18$ cm^{-1}).[6,10,12]

In conclusion, it has been confirmed that the exchange couplings for phenoxo-bridged metal(II) systems (Cu(II), Ni(II), Co(II), Fe(II)) are affected by the *s*/*p* character of the hybrid orbitals (ψ, θ, ϕ) on the bridging oxygen atom by the electronic effects (pK_a and pK_π) of the substituents on the aromatic ring, by the ionic radius (R) and acidity (IE) of the metal(II) ion, and by the number of unpaired electrons (S) and *d* character of the hybrid orbitals (τ) on the metal(II) ion.

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