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NaCl-Type Frameworks of [M(pyrazine)$_2$NO$_2$]ClO$_4$ (M = Co, Cu), the First Examples Containing $\mu_{1,3}$-Nitrito Bridges Showing Antiferromagnetism

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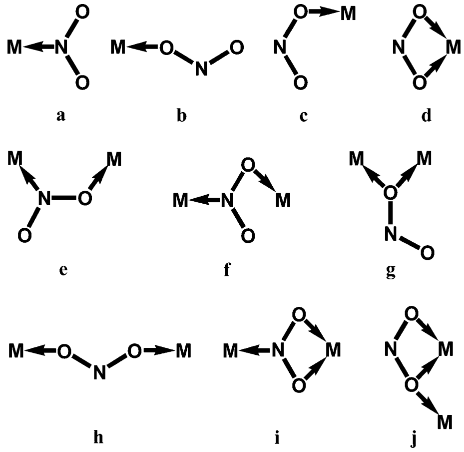
Two new 3D NaCl-type frameworks of [M(pyrazine)$_2$NO$_2$]ClO$_4$ (M = Co, Cu), consist of (4, 4) sheets of metal–pyrazine connected by $\mu_{1,3}$-nitrito, representing the first examples of $\mu_{1,3}$-nitrito bridges and exhibiting antiferromagnetism.

The nitrito group (NO$_2^-$) is unique among the short ligands because it can coordinate metal ions in a variety of ways[1] (Chart 1) in which several are not observed for other ligands (Chart 1e,f,i). As a monodentate ligand, it can use either N or O atoms (Chart 1a−c), while as a bidentate ligand, four modes have been observed (Chart 1d−g), chelating or bridging either through both N and O or through O only, and as a tridentate ligand (Chart 1i, j), it can chelate one metal through two O atoms and bridge another via a N or O atom. Many polynuclear compounds, such as dinuclear,[2] trinuclear,[2a,3] pentanuclear,[4] heptanuclear,[5] and 1D polymeric ones,[6] have been synthesized and characterized, and magnetic-mediating characters of the bridging nitrite have been investigated. For example, the two-atom O/N-bridging mode (Chart 1e) shows moderate antiferromagnetic interaction as observed in several 1D Ni^{2+} chains,[6c,g,i] while a Ni−Mn−Ni trinuclear complex involving the same bridging nitrite as well as azido bridges was reported to show ferromagnetic behavior.[3c] For the single-atom O bridge mode (Chart 1g), weak ferromagnetic interaction was found in a dinuclear Cu^{2+} complex.[2d] The tridentate mode (Chart 1j) displays moderate antiferromagnetic interaction in a dinuclear Ni^{2+} compound[2b] with a combination of chelation at one Ni^{2+}, while the same mode mediates very weak antiferromagnetic interaction in an alternating Cu^{2+} chain[6j] together with bridging oxamidato and nitrito ligands, and a very weak ferromagnetic interaction was observed in a Ni−Cu bimetallic chain[6k] with bidentate nitrito coordination at Ni^{2+}. In despite of these reports, to

Chart 1. Different Coordination Modes of the Nitrite Ion Observed in Literatures Where Mode h Is Reported for the First Time in This Work



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the best of our knowledge, no 2D or 3D polymeric complexes containing nitrito bridges have been documented. On the other hand, pyrazine (pyz) is of benefit for constructing high-dimensional frameworks because it is a good linker as well as a magnetic mediator. Many magnetic systems involving pyz and other short ligands such as cyanide,[7] azide,[8] diacyanamide,[9] and formate[10] have been explored. In this work, we utilize pyz with nitrite to explore whether high-dimensional frameworks can be obtained. Reported here are two new 3D NaCl-type frameworks of $[M(pyz)_2NO_2]ClO_4$ (**1Co**, M = Co; **2Cu**, M = Cu), consisting of (4, 4) sheets of metal−pyz linked by $\mu_{1,3}$-nitrito bridges. They are the first examples of a nitrite ion in this bridging manner (Chart 1h). Both materials are antiferromagnets.

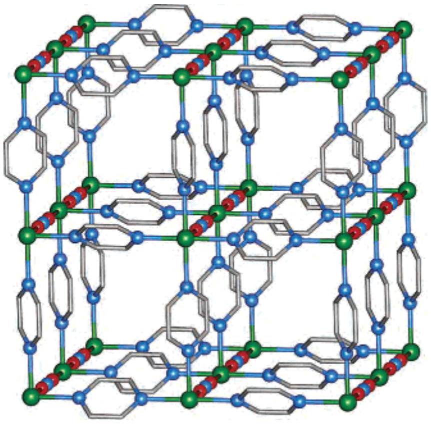

Figure 1. 3D structure of $[M(pyz)_2NO_2]ClO_4$ viewed roughly down the *c* axis. Color scheme: M, green; N, blue; O, red; C, gray. H atoms and ClO_4^- anions were omitted for clarity.

The reaction of metal salts, $Co(ClO_4)_2{\cdot}6H_2O$ for **1Co** and $Cu(ClO_4)_2{\cdot}6H_2O$ for **2Cu**, $NaNO_2$, and pyz produced crystals of the two isomorphs[11] whose structures were determined by X-ray diffraction.[12] The structure (Figures 1 and S1 of the Supporting Information) consists of metal−pyz (4, 4) layers parallel to the *ab* plane further linked by $\mu_{1,3}$-nitrito along the *c* direction, affording a NaCl-like framework, with ClO_4^- lying in the cubic cavities. To the best of our knowledge, this is the first time that the $\mu_{1,3}$-nitrito bridge (Chart 1h) is observed. In both structures, there is only one unique M^{2+} center possessing a slightly compressed (**1Co**) or elongated (**2Cu**) octahedral environment, with the four N atoms of the pyz ligands in the equatorial plane and the two O atoms of the nitrito groups at the apical positions. The unique M−N/O bonds are 2.160/2.068 Å (**1Co**) and 2.049/2.285 Å (**2Cu**), and all N/O−M−N/O angles are ideal 90 or 180°. The O−N−O angle of NO_2^-, in the structures, is 180°, not bent as documented.[1−6] However, the flat, disklike thermal ellipse of N/O atoms (Figure S1a of the Supporting Information) revealed the bent characteristic of NO_2^-. The thermal ellipses have their long axes ($U_{11} = U_{22}$, the principal mean-square atomic displacements) perpendicular, while the short one (U_{33}) parallel to the M···M line or the 4-fold axis, and the ratio of U_{11}/U_{33} is ca. 3 and 7 for the O and N of NO_2^-, respectively (CIF files of the Supporting Information). The NO_2^- group could not be modeled out of the 4-fold axis in the structure calculation. This indicates that the bent NO_2^- locates randomly or rotates around the M···M line. The M···M distances spanned by pyz are 7.128 Å (**1Co**) and 6.877 Å (**2Cu**), while those via NO_2^- are 6.199 Å (**1Co**) and 6.646 Å (**2Cu**). The pyz ring is titled toward the MN_4 basal plane, with the titling angles being 55.0° (**1Co**) and 59.7° (**2Cu**). The ClO_4^- anion in the cubic cavity (Figure S1b of the Supporting Information) forms weak H bonding of O···H−C with pyz, with C···O distances of ca. 3.3 Å and C−H···O angles of 133°. It seems that the ClO_4^- anion plays an important templating role in the formation of the framework.

The magnetic susceptibilities of **1Co** and **2Cu** measured under 1 kOe field are represented in Figure 2. At room temperature, the χT values are 3.18 cm^3 K mol^{-1} for **1Co** and 0.51 cm^3 K mol^{-1} for **2Cu**, being close to those expected for Co^{2+} with $S = {}^3/_2$ and Cu^{2+} with $S = {}^1/_2$.[13] Upon cooling, the χT values decrease more and more rapidly for both complexes, indicating antiferromagnetic behavior. The maxima of χ are observed at 9.4 K for **1Co** and 6.7 K for **2Cu**, suggesting antiferromagnetic ordering. The Neel temperatures, T_N's, determined by the peaks of $d(\chi T)/dT$, are 6.0 K for **1Co** and 4.0 K for **2Cu**. The field-dependent magnetizations (Figure 2, inset), even at 2 K and 50 kOe, being 0.47

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(11) **1Co**: A 5 mL methanol solution containing 0.50 mmol (0.183 g) of $Co(ClO_4)_2{\cdot}6H_2O$ was put in one side of an H-shaped tube. In another side is a 5 mL methanol solution of 1.0 mmol (0.069 g) of $NaNO_2$ and 0.50 mmol (0.040 g) of pyz. 3 mL 2-propanol was carefully layered upon both solutions to allow slow diffusion. A total of 15 mg of orange-red crystals was harvested 1 month later and washed with methanol, yield 16% upon pyz. Anal. Calcd for $C_8H_8ClCoN_5O_6$: C, 26.36; H, 2.21; N, 19.21. Found: C, 25.9(3); H, 2.8(2); N, 18.1(4). The deviation of the found values from the calculated ones indicates a small amount of impurity of ca. 5−6%; see the Supporting Information for further details. IR (cm^{-1}): 3500brw, 3122w, 1602m, 1425vs, 1223m, 1162w, 1116m, 1099vs, 1084vs, 987w, 806m. **2Cu**: A 6 mL water solution of 1.0 mmol (0.371 g) of $Cu(ClO_4)_2{\cdot}6H_2O$ and 1.0 mmol (0.080 g) of pyz was put in one side of an H-shaped tube, while a 6 mL water solution of 4.0 mmol (0.276 g) of $NaNO_2$ was placed in the other side. 3 mL 1,4-dioxane was layered upon both solutions to provide a diffusion pathway. A total of 40 mg of green crystals was obtained 2 weeks later in a yield of 21% upon pyz. Anal. Calcd for $C_8H_8ClCuN_5O_6$: C, 26.03; H, 2.18; N, 18.97. Found: C, 25.97; H, 2.23; N, 18.92. IR (cm^{-1}): 3113w, 1427vs, 1232m, 1159w, 1122m, 1100vs, 1088vs, 987w, 815m.

(12) Crystal data for **1Co**: $M_r = 364.57$, tetragonal, space group *P*4/*nbm*, $a = 10.0812(2)$ Å, $b = 10.0812(2)$ Å, $c = 6.1990(2)$ Å, $V = 630.01(9)$ Å^3, $Z = 2$, $D_c = 1.922$ g cm^{-3}, $\mu = 1.612$ mm^{-1}, 10 797 measured data, 398 unique, $R_{int} = 0.0466$. R1 = 0.0359 for 328 observations of $I \geq 2\sigma(I)$, wR2 = 0.1032 for all data, GOF = 1.121. For **2Cu**: $M_r = 369.18$, tetragonal, space group *P*4/*nbm*, $a = 9.7253(2)$ Å, $b = 9.7253(2)$ Å, $c = 6.6458(3)$ Å, $V = 628.57(3)$ Å^3, $Z = 2$, $D_c = 1.951$ g cm^{-3}, $\mu = 1.988$ mm^{-1}, 9792 measured data, 399 unique, $R_{int} = 0.0672$. R1 = 0.0339 for 338 observations of $I \geq 2\sigma(I)$, wR2 = 0.0960 for all data, GOF = 1.119. The intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K.

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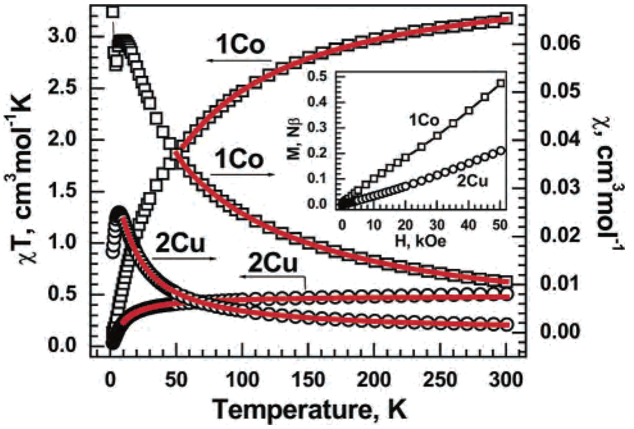

Figure 2. Temperature dependence of the magnetic susceptibility of **1Co** and **2Cu** under an applied field of 1 kOe with the best-fitting data as red lines. Inset: field-dependent magnetization of **1Co** and **2Cu** at 2.0 K.

Nβ (**1Co**) and 0.21 Nβ (**2Cu**), far from the saturated values, confirm the significant antiferromagnetic interactions in both materials. The ac susceptibility data (Figure S2 of the Supporting Information) for both materials show broad maxima in the in-phase components while almost no out-of-phase response, indicating the long-range antiferromagnetic ordering. The rise in χ and the in-phase component of **1Co** below 3 K is probably due to the small amount of impurity in the sample.[11]

Regarding the structure feature, two magnetic exchange pathways are possible: via pyz and $\mu_{1,3}$-nitrito. For **1Co**, the Lines model[14] for a 3D simple cubic lattice was found to fit the high-temperature magnetic data best, though 2D quadratic-layer[14] or 1D Fisher[15] models could be used (see the Supporting Information). Therefore, the 3D model with $H = JS_i \cdot S_j$ was applied, where the impurity was considered as a Curie paramagnetic contribution.[16] The best fitting of the magnetic data above 50 K gave $J = -4.26(2)$ cm^{-1} and $g = 2.790(3)$ with an agreement factor of $R = 7.9 \times 10^{-6}$ ($R = \Sigma(\chi_o - \chi_c)^2/\Sigma\chi_o^2$). The J value means that in **1Co** the coupling between Co^{2+} ions via a pyz bridge is several times larger than those of the previous studies,[17] though it is an average coupling intermediated by both pyz and $\mu_{1,3}$-nitrito. This might be due to the shorter Co$-$N$_{\mathrm{pyz}}$ bond in **1Co**.

For **2Cu**, the case is different. It has been proposed that, for pyz-bridged Cu^{2+} systems where the magnetic orbital is d$_{x^2-y^2}$, the overlap between the d$_{x^2-y^2}$ orbital and the pyz π orbitals determines the magnitude of the antiferromagnetic exchange interaction.[18] The CNDO/2 calculation showed that the π(b$_{1g}$) orbital is the highest-occupied pyz π molecular orbital and mainly C-characterized.[18a,19] If the pyz ring is coplanar with the Cu^{2+} basal plane, the π system of pyz would be orthogonal to the d$_{x^2-y^2}$ orbital and antiferromagnetic interaction would not be observed. This was invoked as the reason for the absence of an antiferromagnetic exchange interaction in polymeric compound [Cu(pyzA)$_2$(ClO$_4$)$_2$]$_n$, where pyzA is pyrazine-2-carboxamide.[20] Titling of the pyz ring relative to the basal plane leads to a possible overlap of the pyz π orbitals with the Cu d$_{x^2-y^2}$ orbital. This case was observed for polymeric [Cu(NO$_3$)$_2$(pyz)]$_x$, where the pyz ring is 50° titled to the Cu basal plane.[18a] The compound shows an antiferromagnetic interaction with $J = -7.4$ cm^{-1}.[18b] In Cu(pyz)$_2$(ClO$_4$)$_2$, the titling angle of 66.1° leads to an antiferromagnetic interaction of $J = -5.3$ cm^{-1}.[21] In **2Cu**, the elongated octahedron of Cu^{2+} indicates that the magnetic orbital is d$_{x^2-y^2}$, whereas the $\mu_{1,3}$-nitrito ligands are at the apical positions. Consequently, the interaction between two magnetic orbitals of Cu ions through $\mu_{1,3}$-nitrito is expected to be weak. On the basis of the above analysis, **2Cu** can be magnetically considered as square layers of Cu$-$pyz. Therefore, χ data of **2Cu** above 10 K were fitted by Lines' quadratic-layer antiferromagnet model with $H = JS_i \cdot S_j$ (see the Supporting Information).[14] The best fitting produced $J = -6.19(3)$ cm^{-1} and $g = 2.288(7)$ with $R = 3.4 \times 10^{-5}$ (R defined as before). The J value is comparable to the aforementioned ones.[18b,21]

In conclusion, we have synthesized two new magnetic 3D NaCl-like networks in which the metal ions are linked by pyz into (4, 4) sheets and further linked by a $\mu_{1,3}$-nitrito group. They provide the first examples containing a $\mu_{1,3}$-nitrito bridge. Furthermore, magnetic investigation reveals that the $\mu_{1,3}$-nitrite bridge can transmit antiferromagnetic interaction in the case of Co^{2+}. To understand the magnetic-mediating character of this new $\mu_{1,3}$ bridge, more homo- or heterometal complexes containing $\mu_{1,3}$-nitrito bridges should be synthesized and characterized, and endeavors are in progress along this line.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1Co** and **2Cu** and Figures S1 and S2 and additional information (PDF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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