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A New Class of Layered Microporous Materials: Crystal Structure of Disodium Pentakis(trimethylphenylammonium) Bis[tris(oxalato(2−))chromate(III)] Chloride Pentahydrate

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Recently, $(Bu_4N)M[Cr(ox)_3]$ (M = Co(II), Cu(II), Fe(II), Mn(II), Ni(II), Zn(II)) were prepared and shown to have interesting Cr−Cr magnetic interactions.[1,2] Although the X-ray structures of these complexes were not determined, both two-dimensional layered networks or three-dimensional networks, with M^{2+} bridges between $[Cr(ox)_3]^{3-}$ complexes were considered. It was deduced that three-dimensional-network structures were more likely[2] on the basis of calculations of potential structures and an analysis of the physical properties of the materials. However, the speculation that two-dimensional networks could be formed from $[Cr(ox)_3]^{3-}$ units[2] has prompted us to report on our earlier work on the first preparation and characterization of members of this new class of materials.[3] The title material has a two-dimensional layer network in which the pores within a layer have the same chirality but alternating layers have opposite chirality, leading to an achiral material. By the use of resolved starting materials or chiral templates, it is likely that chiral materials of this class of materials can be prepared and may have applications in chiral separations, chiral syntheis, and catalysis.

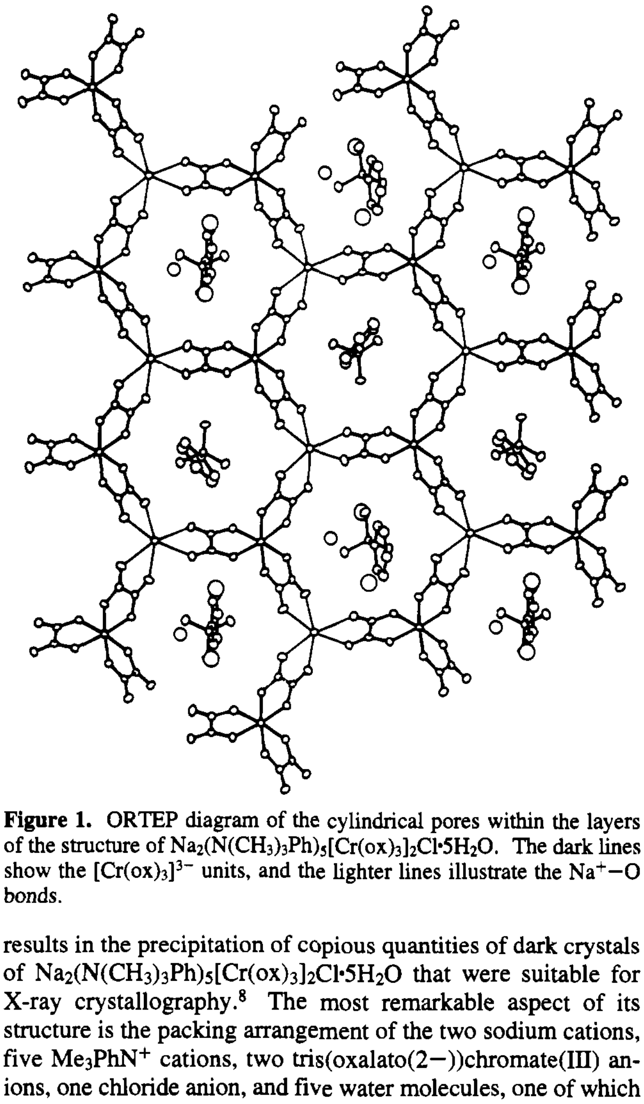

Figure 1. ORTEP diagram of the cylindrical pores within the layers of the structure of $Na_2(N(CH_3)_3Ph)_5[Cr(ox)_3]_2Cl{\cdot}5H_2O$. The dark lines show the $[Cr(ox)_3]^{3-}$ units, and the lighter lines illustrate the Na^+−O bonds.

The relatively-stable Cr(V) complex $[Cr(ehba)_2O]^-$ (ehba = 2-ethyl-2-hydroxybutanoato(2−))[4] undergoes rapid ligand-exchange reactions with oxalate.[5-7] The Cr(V) ligand-exchange products of this reaction in 50% aqueous acetic acid are extracted into CH_2Cl_2 (after the addition of Me_3PhNCl),[3,6] and the extract is allowed to evaporate slowly at room temperature. Over a period of about a day, the brown solution of Cr(V) complexes turns into a green solution of Cr(III) complexes and results in the precipitation of copious quantities of dark crystals of $Na_2(N(CH_3)_3Ph)_5[Cr(ox)_3]_2Cl{\cdot}5H_2O$ that were suitable for X-ray crystallography.[8] The most remarkable aspect of its structure is the packing arrangement of the two sodium cations, five Me_3PhN^+ cations, two tris(oxalato(2−))chromate(III) anions, one chloride anion, and five water molecules, one of which is disordered over two sites. The Na^+ ions are surrounded in a distorted octahedral fashion by six noncoordinated oxygen atoms of the complex anions. This results in the formation of

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(1) Zhong, Z. J.; Matsumoto, N.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 87−90.

(2) Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 6974−6979.

(3) The compound was first mentioned by: Farrell, R. P. B.Sc.(Hons.) Thesis, University of Sydney, 1987. However, no details have been reported.

(4) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 1287−1296.

(5) Farrell, R. P.; Judd, R. J.; Lay, P. A.; Bramley, R.; Ji, J.-Y. *Inorg. Chem.* **1989**, *28*, 3401−3403.

(6) Bramley, R.; Farrell, R. P., Ji, J.-Y.; Lay, P. A. *Aust. J. Chem.* **1990**, *43*, 263−279.

(7) Farrell, R. P.; Lay, P. A. *Comments Inorg. Chem.* **1992**, *13*, 133−175.

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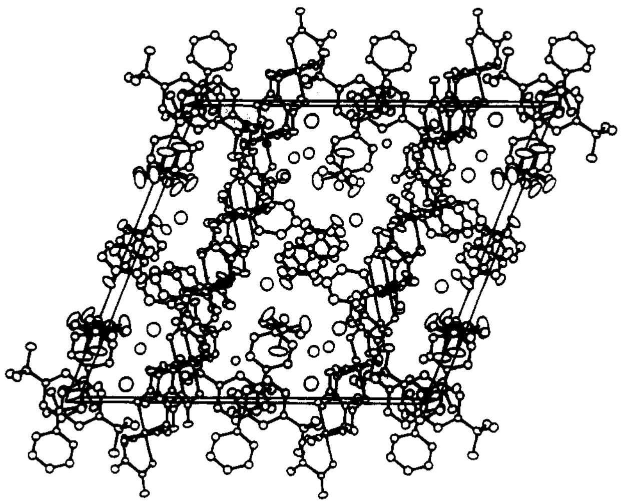

Figure 2. ORTEP diagram of the unit cell depicting the layered structure of $Na_2(CH_3)_3Ph)_5[Cr(ox)_3]_2Cl{\cdot}5H_2O$.

large open pores that are in turn linked to form sheets lying in the *xy* planes at $z = 0.25$ (Figure 1). Lying in the center of about half of these large rings are Me_3PhN^+ cations, while the remainder are empty with a trimethyl group capping one end. It is probable that the presence of bulky "template" cations is required for the formation of the rings that constitute the pores of the microporous materials. Between the sheets are layers of Me_3PhN^+ cations, chloride anions, and water molecules to give a pillared layer structure, in which the some of the organic cations also act as pillars between the layers (Figure 2). There are numerous hydrogen bonds between the chloride anion and the water molecules and between the water molecules themselves.

The $[Cr(ox)_3]^{3-}$ anions have a near-octahedral geometry, but the O−Cr−O angles subtended by the oxalate ligand are significantly less than 90° (mean 82°), which results in distortion from perfect octahedral geometry. This distortion is best expressed as the twist angle[9] which has a value of 30° for a perfect octahedron but is 26.2° in the structure described here. While this is very close to that expected on the basis of the ligand bite size of the ligand,[9] it is significantly different from the value of 23.9° observed in the structure of $K_3[Cr(ox)_3]{\cdot}3H_2O$,[10] suggesting that formation of the rings induces some distortion. The average Cr−O bond length, 1.965(9) Å, is not significantly different from that observed for the potassium salt of 1.969(13) Å.[10]

The coordination geometry about the sodium ions is also best described as distorted octahedral with an average Na−O bond length of 2.41(7) Å, though the smaller bite, which is a consequence of the longer Na−O bonds, results in a smaller twist angle of 21.1°. The C−O bond lengths are similar to those observed in the structure of the $K_3[Cr(ox)_3]{\cdot}3H_2O$,[10] indicating that coordination to the Na^+ cations does not influence these distances and suggesting that the Na−O interactions are primarily electrostatic in nature.

The most important feature of the structure of $Na_2[N(CH_3)_3Ph]_5[Cr(ox)_3]_2Cl{\cdot}5H_2O$ is that it is the first member of a new class of microporous layered materials. Thus, within the layers of Na^+ and $[Cr(ox)_3]^{3-}$ ions, large cylindrical cavities are present that have a diameter of approximately 7 Å and a depth of 3 Å. In the structure, these cavities are occupied partially by $N(CH_3)_3Ph^+$ counterions, while others are empty with a trimethyl group capping one end of the pore. A series of related layered microporous materials have now been prepared by a variety of more rational routes.[11] These involve reactions between an organic template and $M'_3[M(ox)_3]$, which is isolated separately or is generated *in situ* by the reduction of high-oxidation-state metal ions in the presence of oxalic acid. Moreover, partial removal of the templates from these materials by room-temperature cation exchange and complete removal by thermal methods (in addition removal of the waters of crystallization) have been achieved. In both cases, this occurs without loss of crystallinity, apart from some cracking. While the diffraction data obtained to date from these crystals are not of sufficient quality to solve the structures, the above factors point to the integrity of the structures being maintained. Even if the microporous layered structures are disrupted by thermal removal of the template, the ease with which they undergo room-temperature cation exchange, in which bulky template is partially removed, and the fact that half of the pores are empty in the original structures offer the possibilities of using the materials in chiral separations (for materials prepared from resolved complexes). Details of the synthesis, structures, and thermal and ion-exchange properties of these materials will be reported elsewhere.[11]

Acknowledgment. We are grateful for financial support from Australian Research Council and University of Sydney Research Grants.

Supplementary Material Available: Tables of crystal data, positional parameters, bond lengths and bond angles, thermal parameters, hydrogen positional and thermal parameters, deviations from least-squares planes, and close intermolecular contacts (22 pages). Ordering information is given on any current masthead page.

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(8) Intensity data were collected on an Enraf-Nonius CAD4F four-circle diffractometer in the range $1 < \theta < 23°$ using an $\omega-\theta$ scan. Of the 7918 independent reflections collected, 5409 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations. The structure was solved by direct methods using SHELX-76 (Sheldrick, G. M. *SHELX-76: A Program for X-ray Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976), and the solution was extended by difference Fourier methods. Hydrogen atoms were included at calculated sites (C−H = 0.97 Å), and phenyl rings were included as rigid groups (C−C = 1.395 Å). Refinement converged (all shifts $<0.10\sigma$) with $R = 0.059$, $R_w = 0.068$, and $w = 2.26/(\sigma^2(F_o) + 0.00035F_o^2)$. Maximum excursions in a final difference map were +1.0 and −0.40 e $Å^{-3}$. Scattering factors and anomalous dispersion terms used were those supplied in SHELX-76. All calculations were carried out using SHELX-76, and plots were drawn using ORTEP (Johnson, C. K. *ORTEP: A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN 1965). Listings of final atomic coordinates, bond lengths and bond angles, hydrogen atom coordinates and thermal parameters close nonbonded contacts, and details of least-squares planes calculations are deposited as supplementary material. Crystal data: formula $C_{57}H_{80}ClCr_2N_5Na_2O_{29}$; *M* 1484.7; monoclinic, space group $P2_1/c$, *a* 19.665(3), *b* 16.966(7), *c* 22.233(9) Å; β 111.45(3)°; *V* 6904 $Å^3$; *Z* 4; D_c 1.428 g cm^{-3}; μ(Mo Kα) 4.39 cm^{-1}; λ(Mo Kα) 0.7107 Å; *F*(000) 3104 electrons.

(9) Kepert, D. L. *Inorg. Chem.* **1972**, *11*, 1561−1563.

(10) Taylor, D. *Aust. J. Chem.* **1978**, *31*, 1455−1462.

(11) Codd, R.; Cusick, J.; Farrell, R. P.; Hambley, T. W.; Lay, P. A.; Powell, D. W. Manuscripts in preparation.