Synthesis and characterization of $Co_3(O_2CCH_2CH_2PO_3)_2{\cdot}6H_2O$, a metal carboxylate–phosphonate with a framework structure

Anne Distler and Slavi C. Sevov*†

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

The title compound is the first carboxylate–phosphonate with an extended three-dimensional structure, a framework of trimers of edge-sharing CoO_6-octahedra and organic species with two different functional groups, carboxylic and phosphonic, both coordinated to the metal atoms.

The use of multifunctional ligands for building infinite frameworks by coordination to metal centers has become an area gaining much interest in recent years.[1] Many such crystalline coordination polymers with two- and three-dimensional structures are already known for polynitrilies and polyamines coordinated to noble metals.[2] Similarly, polycarboxylic acids,[3] polyalcohols and polyethers,[4] and polyphosphonic acids,[5] have been used for the construction of such solid-state architectures through coordination to a variety of transition metals. Compounds utilizing organic species with two different functional groups, both coordinated to metal atoms, are very rare. Known are an aminophosphonate with an open-framework type structure,[6] and two layered compounds based on carboxylate–phosphonates.[7] Owing to the directionality of the coordination bond, most of these structures have relatively large voids, and are of potential interest for a variety of guest–host interactions and molecular recognition. A common problem for many of them, especially those with long bridging ligands, is the interpenetration of the frameworks which essentially results in blocking the otherwise available large openings. As far as thermal stability is concerned the phosphonates tend to be the more stable group. We are interested in combining two or more different functionalities in a single compound with a three-dimensional open-framework structure. Here we report on a carboxylate–phosphonate compound with such an extended framework built of transition metals coordinated by a bridging ligand with two different functional groups.

The title compound was initially made in an autoclave at 110 °C from $CoCO_3$ and 2-carboxyethylphosphonic acid, $HO_2CCH_2CH_2P(O)(OH)_2$, mixed in a molar ratio of 2 : 1. The synthesis can be also carried out in an open system as low as 80 °C. The compound crystallizes as spherical aggregates of red-purple crystals. A single crystal structure determination‡ revealed a three-dimensional network of linear trimers of edge-sharing CoO_6-octahedra with the organic molecules coordinated to the cobalt atoms by both functional ends (Fig. 1). The cobalt atoms are of two types, Co2 at an inversion center at the center of the trimer, and Co1 inside the other two octahedra (Fig. 2). The Co2-octahedron shares the two opposite parallel edges, O1 and O6, with the Co1-octahedra. The latter are rotated in opposite directions around the common edges keeping the three cobalt atoms in a straight line. This leads to shorter distances between some of the apical oxygen atoms, O2 and O3. These and one of the shared oxygens, O1 from an adjacent trimer, are bonded to a single phosphorus atom.

The acidic oxygens of both functional groups are fully deprotonated. The carboxy group is coordinated to Co1 as a monodentate ligand through its deprotonated oxygen atom leaving the 'double'-bonded oxygen, O5, as non-bonding (Fig. 2). Thus an extended structure of covalently bonded network –Co–O–P–C–C–C–O–Co– is formed. This network has one-dimensional, S-shaped voids filled with the water molecules, O6, 7 and 8 (Figs. 1 and 3). The latter complete the octahedral coordination sphere around the cobalt atoms by

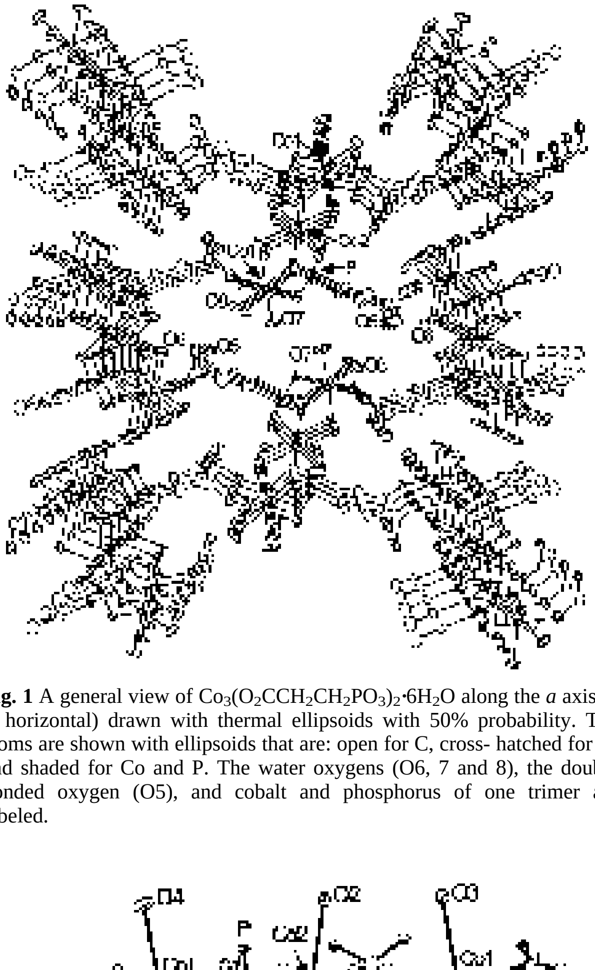

Fig. 1 A general view of $Co_3(O_2CCH_2CH_2PO_3)_2{\cdot}6H_2O$ along the *a* axis (*c* is horizontal) drawn with thermal ellipsoids with 50% probability. The atoms are shown with ellipsoids that are: open for C, cross- hatched for O, and shaded for Co and P. The water oxygens (O6, 7 and 8), the double bonded oxygen (O5), and cobalt and phosphorus of one trimer are labeled.

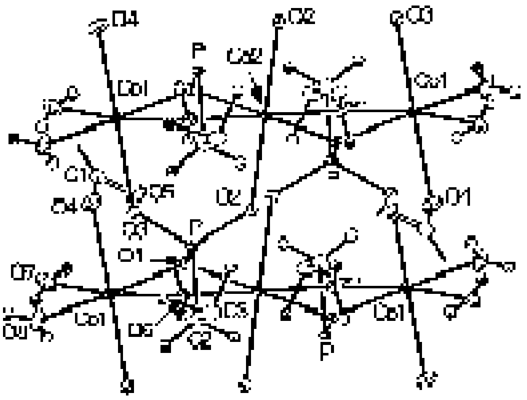

Fig. 2 A closer view of the bonding within and between the trimers of edge-sharing octahedra. Selected distances (Å): Co1–O1 2.066(4), Co1–O3 2.057(3), Co1–O4 2.105(4), Co1–O6 2.215(4), Co1–O7 2.098(4), Co1–O8 2.052(5), Co2–O1 2.098(3), Co2–O2 2.059(3), Co2–O6 2.168(4), P–O1 1.545(4), P–O2 1.517(4), P–O3 1.525(4), P–C2 1.807(6), C1–C2 1.509(8), C2–C3 1.516(9), C1–O5 1.260(7), C1–O4 1.267(7).

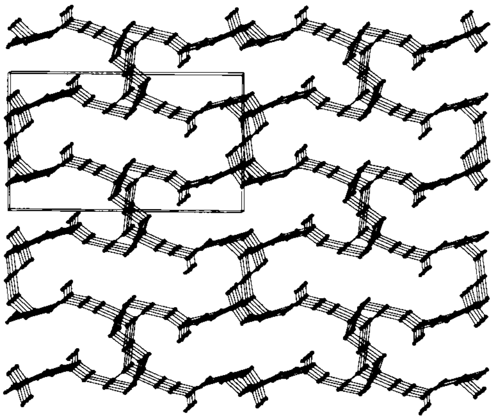

Fig. 3 A view along *a* (as in Fig. 1) of the compound with the water molecules omitted for clarity. The S-shaped one-dimensional openings are easier to see. This is what the dehydrated compound may look like.

coordinating to either one (O7 and O8 to Co1) or two (O6 to both Co1 and Co2) of them.

The IR spectrum of the compound shows the asymmetric and symmetric vibrations of the carboxy group at 1541 and 1419 cm^{-1}, respectively, the vibrations of the phosphonic group in the region 900–1100 cm^{-1}, and the typical bands of the coordinated water (broad at 3369 and sharp at 1646 cm^{-1}). The absence of a band in the region 1690–1730 cm^{-1} (the O–H vibration of a CO_2H group) is in agreement with a deprotonated carboxy group. Magnetic susceptibility measurements in the range 10–300 K show a Curie-type paramagnetism consistent with the structure of 'isolated' islands of cobalt trimers ($\mu = 9\ \mu_B$). A mass loss of 17.5% was measured by TG at *ca.* 150 °C, and this is consistent with six molecules of water (also confirmed by IR after the dehydration). At that temperature the sample changes color from purple to an intense blue, and this confirms the lowering of the cobalt coordination number. Fig. 3 depicts the structure of the compound without the water molecules. Based on the van der Waals radii, the calculated free volume per unit cell of the treated compound is *ca.* 190 Å^3, or 23% of the total volume.§

This new compound provides potential for further explorations. For example, it may be possible to replace the water molecules with different amines. Also, the fact that the C=O part of the carboxylic acid is 'intact' can eventually be used for reactions with different organic molecules with catalytic, photoelectric, or other useful properties in order to 'anchor' them to the solid.

We thank the National Science Foundation (DMR-9701550) for the financial support.

Notes and References

† E-mail: ssevov@nd.edu

‡ *Crystal data* for $Co_3(O_2CCH_2CH_2PO_3)_2\cdot 6H_2O$: $M_w = 586.95$, monoclinic, space group $P2_1/c$, $Z = 2$, $a = 4.6086(9)$, $b = 10.278(3)$, $c = 17.504(3)$ Å, $\beta = 95.74(1)°$, $U = 825.0(3)$ Å^3, $\mu = 32.61\ cm^{-1}$. A hemisphere of data was collected on a CAD4 single crystal diffractometer with graphite-monochromated Mo-Kα radiation at room temperature (crystal size $0.04 \times 0.08 \times 0.10$ mm, ω–2θ scans, 2998 and 1455 collected and independent reflections ($R_{int} = 7.87\%$), respectively). The structure was solved by direct methods and refined with the aid of the SHELXTL-V5.0 package. All lighter atoms, including hydrogen, were located from difference Fourier maps, and refined without constraints. XABS empirical absorption correction was applied to the data after the structure was refined with isotropic thermal parameters. Final residual values: $R_1/wR_2 = 0.0498/0.1036$ for 1185 observed reflections ($I \geqslant 2\sigma_I$) and 163 refined parameters ($R_1/wR_2 = 0.0634/0.1114$ for all data). CCDC 182/825.

§ While the manuscript was being reviewed we made and characterized two more metal carboxylate–phosphonates, an isostructural magnesium analog [$a = 4.598(2)$, $b = 10.278(4)$, $c = 17.628(7)$ Å, $\beta = 96.28(3)°$, $U = 828.1(4)$ Å^3] and a calcium carboxylate–phosphonate with a different structure. According to the structure determined from single crystal X-ray diffraction and IR spectra of the latter, the calcium is seven-coordinate, and the carboxylic group is not deprotonated but rather coordinated to the calcium *via* the carbonyl oxygen.

1 *Comprehensive Supramolecular Chemistry,* ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Pergamon, New York, 1996, vol. 6 (*Solid-state supramolecular chemistry: crystal engineering*) and vol. 7 (*Solid-state supramolecular chemistry: two- and three-dimensional inorganic networks*).

2 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, ed. T. Bein, ACS Symp. Ser. 499, ACS, Washington, DC, 1992, ch. 19; A. J. Blake, N. R. Champness, S. S. M. Chung, W. S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.

3 O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861; O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096; S. O. H. Gutschke, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 991; K. J. Lin and K. H. Lii, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2076.

4 J. R. Black, N. R. Champness, W. Levason and G. Reid, *Inorg. Chem.*, 1996, **35**, 4432; J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc., Chem. Commun.*, 1995, 1277; J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1995, 3439.

5 D. M. Poojary, B. Zhang, P. Bellinghausen and A. Clearfield, *Inorg. Chem.*, 1996, **35**, 4942; G. Bonavia, R. C. Haushalter, C. J. O'Connor and J. Zubieta, *Inorg. Chem.*, 1996, **35**, 5603; R. LaDuca, D. Rose, J. R. D. DeBord, R. C. Haushalter, C. J. O'Connor and Jon Zubieta, *J. Solid State Chem.*, 1996, **123**, 408; G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1357; V. Soghomonian, R. Diaz, R. C. Haushalter, C. J. O'Connor and J. Zubieta, *Inorg. Chem.*, 1995, **34**, 4460; D. Lohse and S. C. Sevov, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1619.

6 S. Drumel, P. Janvier, D. Deniaud and B. Bujoli, *J. Chem. Soc., Chem. Commun.*, 1995, 1051.

7 S. Drumel, P. Janvier, P. Barboux, M. Bujoli-Doeuff and B. Bujoli, *Inorg. Chem.*, 1995, **34**, 148; S. Drumel, P. Janvier, M. Bujoli-Doeuff and B. Bujoli, *New J. Chem.*, 1995, **19**, 239.

Received in Bloomington, IN, USA, 10th February 1998; 8/01964I