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Poly[[diaquabis[μ_2-2-(4-pyridinio)-propane-1,3-dionato-κ^2O:O']-cobalt(II)] dinitrate]

Konstantin V. Domasevitch

Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev 01033, Ukraine
Correspondence e-mail: dk@univ.kiev.ua

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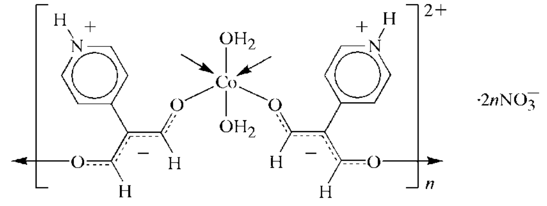
The title compound, $\{[Co(C_8H_7NO_2)_2(H_2O)_2](NO_3)_2\}_n$, is the first *d*-metal ion complex involving bidentate bridging of a β-dialdehyde group. The Co^{2+} ion is situated on an inversion centre and adopts an octahedral coordination with four equatorial aldehyde O atoms [Co—O = 2.0910 (14) and 2.1083 (14) Å] and two axial aqua ligands [Co—O = 2.0631 (13) Å]. The title compound has a two-dimensional square-grid framework structure supported by propane-1,3-dionate *O*:*O*′-bridges between the metal ions. The organic ligand itself possesses a zwitterionic structure, involving conjugated anionic propane-1,3-dionate and cationic pyridinium fragments. Hydrogen bonding between coordinated water molecules, the pyridinium NH group and the nitrate anions [O···O = 2.749 (2) and 2.766 (3) Å, and N···O = 2.864 (3) Å] is essential for the crystal packing.

Comment

In view of providing pathways for magnetic coupling between bridged paramagnetic metal centres, formate complexes (Wang *et al.*, 2005) bear a close resemblance to common azide systems (Cabrero *et al.*, 2003). To sustain long-range magnetic coupling, extended conjugated *O*-donor bridges *M*—O—CH═CH—CH═O—*M* may be formally related to formate compounds as vinylogues. However, this coordination mode of propane-1,3-dionates towards *d*-metal ions is entirely unknown and the formation of such coordination bridges is difficult to predict. Unlike the thoroughly explored chemistry of 1,3-diketones, one of the most common ligand systems, structural information on 1,3-dialdehydes and their metal complexes is extremely scarce. In the anionic magnesium complex $(NMe_4)[Mg\{C(CHO)_3\}_3]$, the triformylmethanide group behaves as a chelate *O*,*O*′-donor (Groth, 1987), while the 2-phenylpropane-1,3-dionate anion is monodentate, or *O*:*O*′-bridging as in the tetraphenylantimony(V) and triphenyltin(IV) compounds (Perrin & Kim, 2000). In two reported *d*-metal complexes, *viz*. chromium(III) tris(propane-1,3-dionate) (Glick *et al.*, 1975) and the tris-complex of Co^{II} with the 2-nitromalonic aldehyde anion (Albertin *et al.*, 1981), the ligands are bidentate chelates, similar to the 1,3-diketonate analogues. We suppose that the *O*:*O*′-bridging coordination of the dialdehyde frame may be more characteristic in the case of formally neutral ligands, while significant conjugation within the diformylmethylide site is possible under deprotonation and therefore the appropriate ligand pattern may be best provided by a zwitterion. Some such charge-separated species cocrystallize even with alkali metal salts (Kolehmainen *et al.*, 1989) and may be viewed as promising ligands for the synthesis of coordination polymers. In this context, we have examined the cobalt(II) nitrate complex with 4-pyridyl-substituted malonic aldehyde, a representative amphoteric ligand possessing relatively strong basic and acidic sites.



(I)

In the title compound, (I), the organic ligand exists as a zwitterion and the molecular framework involves charge-separated anionic 1,3-dionate and cationic 4-pyridinium fragments. The Co^{2+} ion is situated on an inversion centre and adopts a typical sixfold CoO_6 coordination, with a slightly distorted octahedral geometry (Fig. 1). This involves four aldehyde O atoms in the equatorial plane [Co—O = 2.0910 (14) and 2.1083 (14) Å] and two water molecules [Co—

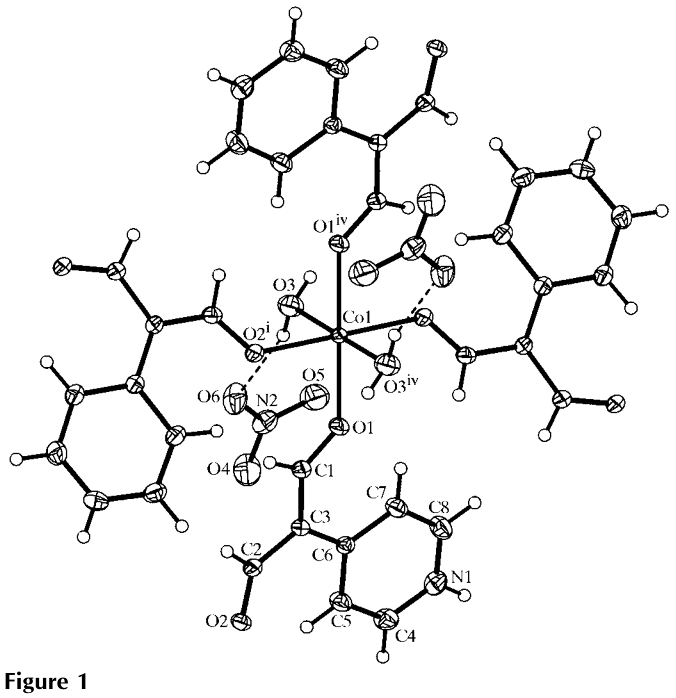


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y, -z$.]

O = 2.0631 (13) Å] in the axial positions (Table 1). Thus, the bond lengths with the axial aqua ligands are even shorter than those formed with the organic donors. The latter act as *O*:*O*′-bidentate bridges between two Co^{2+} ions, separated by 8.26 Å (symmetry code: $-x, y - \frac{1}{2}, -z + \frac{1}{2}$), allowing propagation of the coordination geometry and assembly of a flat four-connected network ('square-grid net') (Fig. 2). It is interesting to note that the topology and shape of the network are very similar to those observed in the 3*d*-metal (Co, Ni) formate complexes with urea (Koyano *et al.*, 1992) and formamide (Domasevitch *et al.*, 2002). This also suggests close structural resemblance of the formate and 1,3-dionate (as the vinylogous formate anion) groups as bridging blocks for the design of polymeric coordination compounds. The space inside the square meshes of the framework is populated with a pair of pyridinium groups of the ligands that show characteristic slipped π–π stacking (Fig. 2). These two heterocycles are related by inversion ($-x, 1 - y, -z$) and are situated parallel to one another with a relatively long centroid-to-centroid distance of 3.705 (2) Å [interplanar distance = 3.482 (2) Å and slippage angle of the interacting groups = 29.92 (2)°] (Janiak, 2000).

The noncoordinated nitrate anions are involved in the overall three-dimensional supramolecular structure of (I) as acceptors of three strong hydrogen bonds with water molecules and pyridinium NH donors (Table 2). Two coordinated water molecules and two nitrate anions assemble into typical centrosymmetric aqua–anion dimers (Fig. 3). Such modes of interaction between the components were also observed in the diaquanickel dinitrate complex with a substituted phenanthroline ligand (Freire *et al.*, 2002). The third O atom of the nitrate anion accepts a hydrogen bond from a pyridinium NH group [$N1\cdots O4^{iii}$ = 2.864 (3) Å; symmetry code: (iii) $1 - x, 1 - y, -z$]. This interaction is slightly weaker than that present in pyridinium nitrate itself ($N\cdots O$ = 2.70 Å; Batsanov, 2004). In total, these hydrogen-bond interactions provide cross-linking of successive coordination layers, which are related by translation along the *a* axis (interlayer separation = 7.57 Å).

The molecular structure of the ligand is planar, with the dihedral angle between the mean planes through the heterocyclic and dialdehyde fragments being 7.6 (2)°. Bond lengths indicate effective delocalization of the π-electron density, since both pairs of C—C [1.418 (3) and 1.422 (2) Å] and C—O [1.240 (2) and 1.249 (2) Å] bonds in the dionate fragment are practically uniform (Table 1). This is consistent with the geometry of the conjugated phenylmalonic dialdehyde anion in its triethylammonium salt and in the triphenyltin(IV) complex (Perrin & Kim, 2000), the only known structural precedent for *O*:*O*′-bridging coordination of dialdehyde. However, monodentate coordination of the latter ligand led to localization of the single and double bonds (*i.e.* C—O = 1.288 and 1.218 Å). The C3—C6 bond between the pyridinium and methylide fragments is also suggestive of conjugation and is shorter than in the structure of the phenyl analogue [1.455 (3) *versus* 1.485–1.493 Å; Semmingsen, 1977]. The O1—C1—C3—C2—O2 chain adopts a *trans*–*trans* configuration (see torsion angles in Table 1), which is the most characteristic arrangement for dialdehyde fragments in crystal structures. It is unlikely to be influenced by possible intramolecular weak C—H$\cdots$O hydrogen bonding [*e.g.* $C7\cdots O1$ = 2.848 (3) Å and $C7-H7\cdots O1$ = 127°], since a similar configuration was

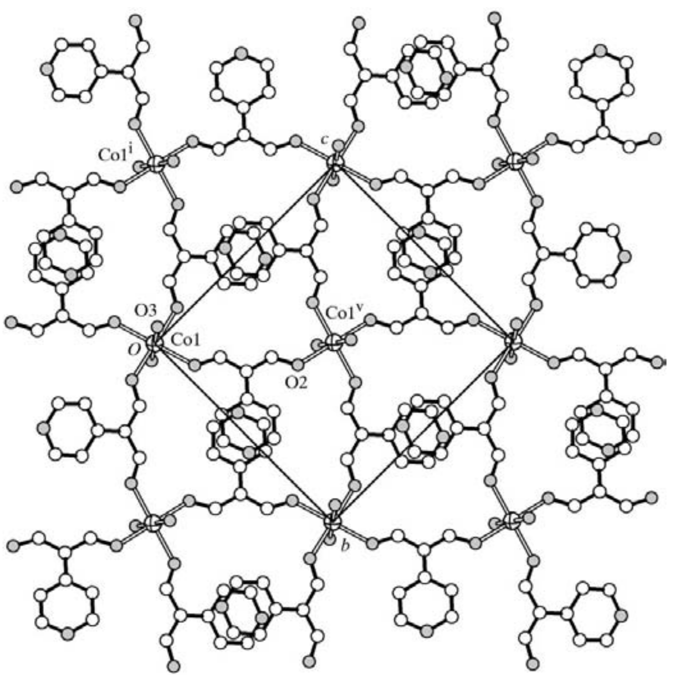


Figure 2
A view of the square-grid network in the structure of (I), showing the bridging coordination of the diformylmethylide fragment and the slipped π–π interaction of the heterocyclic groups situated inside the rectangular cages (projection on to the *bc* plane). H atoms have been omitted for clarity and O and N atoms are shaded grey. [Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.]

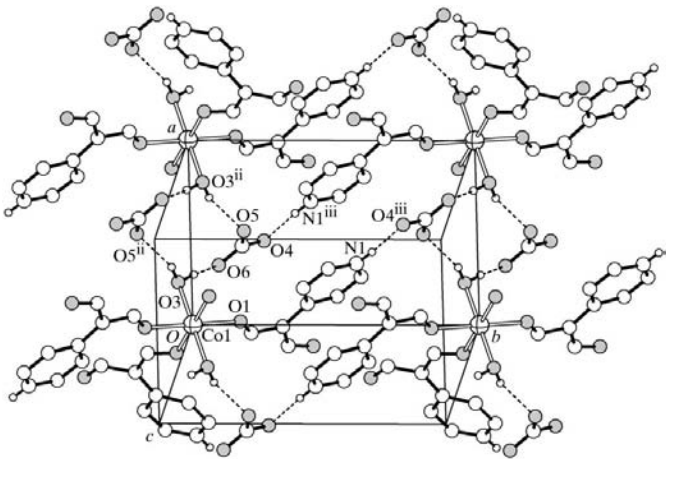


Figure 3
A view of the interconnection of the coordination layers in (I) *via* hydrogen-bonded nitrate anions. Dashed lines indicate hydrogen bonds. Note the formation of the characteristic aqua–anion dimers. C-bound H atoms have been omitted for clarity and O atoms are shaded grey. [Symmetry codes: (ii) $-x + 1, -y, -z$; (iii) $-x + 1, -y + 1, -z$.]

retained even in related molecules with orthogonal disposition of the aromatic and diformylmethylide fragments (Mueller *et al.*, 2001), and in the aliphatic trimethylammonium diformylmethylide (Kolehmainen *et al.*, 1989).

In conclusion, compound (I) provides the first example of diformylmethylide *O*:*O*′-bridges between transition metal ions and it suggests the utility of zwitterionic dialdehydes as highly conjugated ligands for coordination compounds. This may find further application in the development of metal–organic systems with long-range magnetic coupling between paramagnetic metal centres.

Experimental

The 2-(4-pyridyl)propane-1,3-dione ligand was prepared by Vilsmeyer–Haack formylation of 4-methylpyridine (Arnold, 1963). For the synthesis of compound (I), the ligand (0.148 g, 1.0 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.5 mmol) were dissolved in methanol (20 ml). Slow evaporation of the solution at room temperature led to the crystallization of yellow prisms of (I) (yield 70%, 0.18 g).

Crystal data

$[Co(C_8H_7NO_2)_2(H_2O)_2](NO_3)_2$	V = 1033.24 (17) Å^3
M_r = 517.27	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.6156 (8) Å	μ = 0.91 mm^{-1}
b = 11.5530 (9) Å	T = 213 (2) K
c = 11.8140 (11) Å	0.24 × 0.20 × 0.20 mm
β = 96.258 (2)°	

Data collection

Siemens SMART CCD area-detector diffractometer	3557 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2235 independent reflections
$T_{\min}$ = 0.812, $T_{\max}$ = 0.840	1908 reflections with $I > 2\sigma(I)$
	$R_{\rm int}$ = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	151 parameters
$wR(F^2)$ = 0.109	H-atom parameters constrained
S = 1.02	$\Delta\rho_{\max}$ = 0.56 e Å^{-3}
2235 reflections	$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.1083 (14)	O2—C2	1.249 (2)
Co1—O2$^{\rm i}$	2.0910 (14)	C1—C3	1.422 (2)
Co1—O3	2.0631 (13)	C2—C3	1.418 (3)
O1—C1	1.240 (2)	C3—C6	1.455 (3)
O2$^{\rm i}$—Co1—O1	89.29 (6)	O2—C2—C3	127.99 (18)
O3—Co1—O1	90.04 (5)	C2—C3—C1	113.37 (17)
O3—Co1—O2$^{\rm i}$	88.94 (5)	C2—C3—C6	123.44 (16)
O1—C1—C3	128.04 (19)		
O1—C1—C3—C2	176.1 (2)	O2—C2—C3—C1	−178.7 (2)

Symmetry code: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H1$W\cdots$O5$^{\rm ii}$	0.85	2.00	2.766 (2)	149
O3—H2$W\cdots$O6	0.85	1.94	2.749 (2)	158
N1—H1N$\cdots$O4$^{\rm iii}$	0.87	2.00	2.864 (3)	170

Symmetry codes: (ii) $-x + 1, -y, -z$; (iii) $-x + 1, -y + 1, -z$.

H atoms were located in difference Fourier maps and were then treated as riding atoms, with O—H = 0.85 Å, N—H = 0.87 Å and C—H = 0.94 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(O,N).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.700.00; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3015). Services for accessing these data are described at the back of the journal.

References

Albertin, G., Bordignon, E., Orio, A., Pelizzi, G. & Tarasconi, P. (1981). *Inorg. Chem.* **20**, 2862–2868.

Arnold, Z. (1963). *Collect. Czech. Chem. Commun.* **28**, 863–868.

Batsanov, A. S. (2004). *Acta Cryst.* E**60**, o2426–o2428.

Brandenburg, K. (1999). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.

Bruker (1998). *SMART-NT*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT-NT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.

Cabrero, J., de Graaf, C., Bordas, E., Caballol, R. & Malrieu, J.-P. (2003). *Chem. Eur. J.* **9**, 2307–2315.

Domasevitch, K. V., Sieler, J., Rusanov, E. B. & Chernega, A. N. (2002). *Z. Anorg. Allg. Chem.* **51**, 628–633.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Freire, E., Baggio, S., Muñoz, J. C. & Baggio, R. (2002). *Acta Cryst.* C**58**, m221–m224.

Glick, M. D., Andrelczyk, B. & Lintvedt, R. L. (1975). *Acta Cryst.* B**31**, 916–918.

Groth, P. (1987). *Acta Chem. Scand. Ser. A*, **41**, 178–186.

Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3898.

Kolehmainen, E., Laatikainen, R., Rissanen, K., Valkonen, J., Saman, D. & Kral, V. (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. 859–864.

Koyano, N., Fukui, R. S., Iwata, Y. & Shibuya, I. (1992). *Jpn J. Appl. Phys.* **31**, 3559–3565.

Mueller, T. J. J., Gompper, R. & Polborn, K. (2001). Private communication (refcode QULBUU). CCDC, 12 Union Road, Cambridge, England.

Perrin, C. L. & Kim, Y.-J. (2000). *Inorg. Chem.* **39**, 3902–3910.

Semmingsen, D. (1977). *Acta Chem. Scand. Ser. B*, **31**, 114–118.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Wang, X.-Y., Wei, H.-Y., Wang, Z.-M., Chen, Z.-D. & Song, G. (2005). *Inorg. Chem.* **44**, 572–583.