Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonding and π–π stacking interactions in aquachloridobis(1,10-phenanthroline)cobalt(II) chloride dichloridobis(1,10-phenanthroline)-cobalt(II) hexahydrate

Janice M. Rubin-Preminger, Leonid Kozlov and Israel Goldberg*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel
Correspondence e-mail: goldberg@post.tau.ac.il

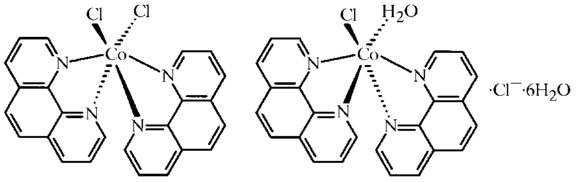
Received 29 October 2007
Accepted 30 November 2007
Online 12 January 2008

The title compound, $[CoCl(C_{12}H_8N_2)_2(H_2O)]Cl\cdot[CoCl_2(C_{12}H_8N_2)_2]\cdot 6H_2O$, is the first example of a new 1:1 cocrystal of the octahedral $[CoCl_2(phen)_2]$ and $[CoCl(phen)_2(H_2O)]^+\cdot Cl^-$ complexes (phen is 1,10-phenanthroline). The latter form heterochiral dimers held by strong π–π stacking interactions *via* their phenathroline ligands, which confirms that π stacking is an important and reliable synthon in supramolecular design. In addition, the crystal structure is networked by $H_2O\cdots H_2O$, $H_2O\cdots Cl^-$ and $H_2O\cdots Cl$ hydrogen bonds, which interconnect the different units of the cobalt complexes.

Comment

Recently, we have been studying supramolecular chemistry based on π–π stacking interactions, involving aromatic units such as 1,10-phenanthroline (phen) and its larger derivatives with extended aromatic systems and ligating capacity, and exploring their coordination chemistry with various transition metals (Bergman *et al.*, 2002, 2004, 2005; Gut *et al.*, 2002). We found, for example, that octahedral complexes of ruthenium and osmium with such ligands tend to dimerize *via* π–π stacking in solution as well as in the solid state. We noted also that metal complexes with phen or modified phen ligands can be useful in diagnostic and therapeutic applications (Barton, 1986; Naing *et al.*, 1995), which adds interest to studies of the structural chemistry of these materials. In the above context, only a small number of reports on the structural chemistry of Co^{II} complexes with phen ligands have been published so far, justifying further studies in this area.

In the present work, we prepared crystals of $[CoCl_2(phen)_2]$ dihydrate (green blocks), (I), of the previously known structure (Ablov *et al.*, 1966; Andersen & Josephsen, 1971) $[CoCl(phen)_2(H_2O)]$ (pink prisms), (II), in good agreement with the literature (Zhao *et al.*, 2003), and of a new 1:1 cocrystal of the two Co–phen complexes in a polyhydrated form (maroon cubes), (III).



(III)

Compound (I) crystallized in an orthorhombic space group [*Pbcn*, with *a* = 12.619 (1) Å, *b* = 23.410 (1) Å and *c* = 176.034 (2) Å], but the analyzed crystals were of poor quality and the structure could not be analyzed with acceptable precision. The crystallographic refinement converged at *R*1 = 0.074, adequately low to identify unequivocally the molecular structure of the complex. It is noteworthy that (I) has unit-cell parameters quite different from those given for the monohydrate [Cambridge Structural Database (Allen, 2002) refcode QQQERJ; *a* = 12.270 Å, *b* = 13.500 Å, *c* = 15.330 Å and *β* = 99.40°; Andersen & Josephsen, 1971] and the trihydrate (refcode CPHCOC; *a* = 15.460 Å, *b* = 13.500 Å, *c* = 12.280 Å and *β* = 90.17°; Ablov *et al.*, 1966). On the other hand, the crystal data for (I) are in good agreement with those published for $[Cr^{III}(phen)_2Cl_2]Cl\cdot 2H_2O$ (QQQEQS; Andersen & Josephsen, 1971). Atomic coordinates are not available in either of the earlier reports, which may reflect the difficulty

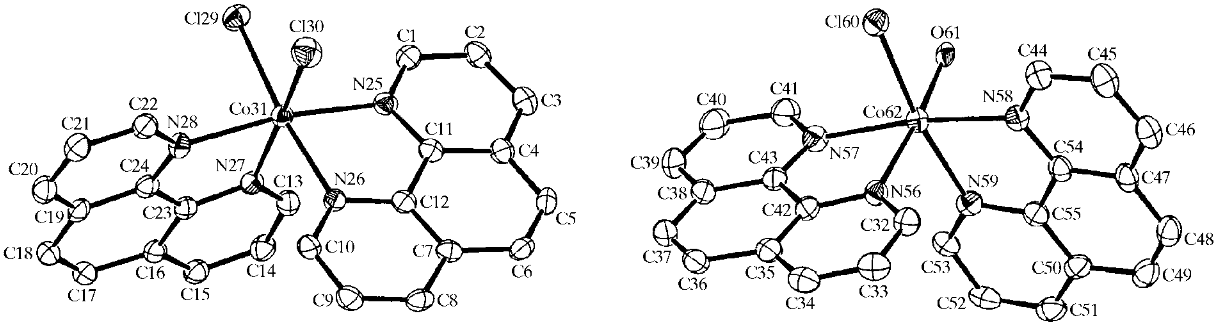


Figure 1
Views of the two cobalt complexes in (III), shown in approximately the same orientation, with the atom-labeling scheme. Ellipsoids represent displacement parameters at the 50% probability level and H atoms have been omitted.

DOI: 10.1107/S0108270107064803

of obtaining good quality crystals of these species, probably as a result of the instability of Co^{II} and the tendency of its complexes to crystallize as solvates.

Compound (II) crystallized in a triclinic space group [$P\overline{1}$, with a = 9.631 (1) Å, b = 11.340 (1) Å, c = 12.958 (1) Å, α = 64.083 (7)°, β = 83.358 (5)° and γ = 78.199 (4)°], in good agreement with the previously reported structure (ESEQO1; Zhao *et al.*, 2003).

Compound (III) is of particular interest as it represents a unique 1:1 cocrystal of the two species [$CoCl_2(phen)_2$] and [$CoCl(phen)_2(H_2O)$]Cl in a hexahydrated form, the structure of which has not been published before. It is the subject matter of the current report. This material was obtained by hydrothermal synthesis, which provides unique crystallization conditions to yield new products that are often inaccessible by standard techniques of crystal growth by evaporation and temperature control. Fig. 1 shows the molecular structure of (III) at 110 (2) K, as observed in this study. In this family of octahedral complexes, the two molecules of the bidentate phen ligand are *cis* to one another, as are the two additional monodentate Cl and H_2O ligands. All the observed cobalt–ligand bond lengths are in good agreement with the literature (Orpen *et al.*, 1989).

The intermolecular interaction of the cobalt complexes *via* aryl–aryl stacking of the phen fragments of the two species is addressed first. Within the asymmetric unit there is partial overlap between the C1–C12/N25/N26 and C44–C55/N58/N59 phen ring systems, with shortest interatomic distances near 3.7 Å. These two ring systems are not fully parallel to one another, the dihedral angle between their mean planes being 16.69 (5)°. An apparently more effective interaction occurs between the phen ring system C13–C24/N27/N28 of one complex and C32–C43/N56/N57 of another complex at ($-x+1$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$). In this case, the two ring systems are quite parallel, the dihedral angle between them being only 1.88 (5)°, with an average distance of 3.26 Å between their mean planes. The overlapping systems are depicted in Fig. 2. These observations confirm that the cobalt complexes with phen are organized as distinct dimers in which the phen residues interact *via* π–π stacking interactions. Moreover, the two interacting complexes are of opposing Δ and Λ chirality, which are not related by inversion. This confirms that heterochiral dimer formation occurs not only in organometallic complexes with large aromatic ligands, as reported earlier (Bergman *et al.*, 2002, 2004, 2005; Gut *et al.*, 2002), but also with the relatively small phen ligand. The crystal structure of (III) is stabilized also by an extended array of O—H···O, O—H···Cl and O—H···Cl hydrogen bonds, through the aqua and Cl ligands as well as the solvent water molecules and chloride anions that interface the coordination complexes (Fig. 3). These interactions are in the normal range (Table 1). The hydrogen bonds link between species that are located in the crystal structure in layered zones centered at (x, 0, z) and (x, $\frac{1}{2}$, z). The hydrogen-bonded layers are stacked along the b axis, with the phen residues of the two complexes lining the interface between them. Fig. 4 shows the projection of the crystal structure approximately down the c axis, illustrating the two perpendicular zones along a and c occupied by columns of the phen fragments.

In summary, a new cocrystal of two different octahedral complexes of Co^{II} has been determined. The observed results confirm the tendency of such octahedral complexes to aggregate in heterochiral dimers *via* π–π stacking interactions, in agreement with our earlier findings with other aromatic components (Bergman *et al.*, 2002, 2004, 2005; Gut *et al.*, 2002). These results indicate also that such chiral recognition is well expressed, not only in chemical systems held solely by π

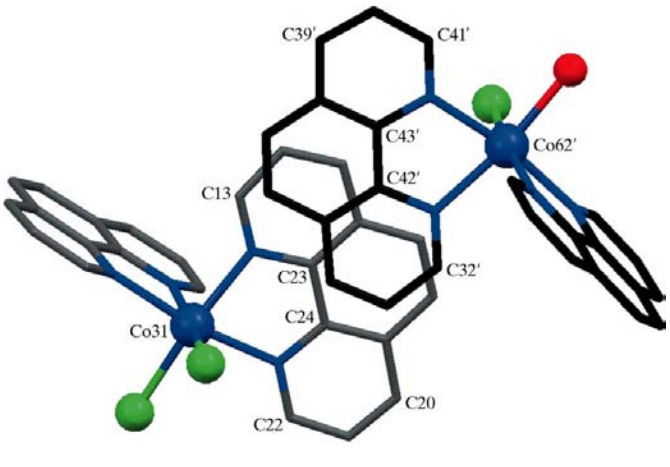


Figure 2
An illustration of the π–π stacking interaction between the two cobalt complexes in (III). Selected atomic labels identify the two interacting components of the dimer. Primed atoms are related to the corresponding atoms of the asymmetric unit by ($-x+1$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$).

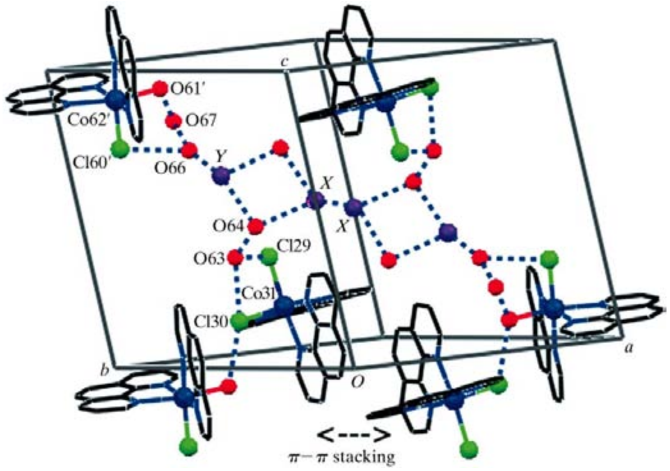


Figure 3
A view of the hydrogen-bonding pattern in (III), denoted by dashed lines. The Co, Cl and O atoms are shown as small spheres. The various atom types that take part in the hydrogen-bonding scheme are labeled. Atoms Co62, O61 and Cl60 are related by ($-x$, $-y+1$, $-z+1$) to those in Fig. 1. Labels X and Y represent the disordered chloride anions and water molecule. X represents in an alternating manner (*i.e.* with 50% occupancy each) atomic positions O68 and Cl70, while Y represents atomic positions O69 and Cl71. H atoms have been omitted for clarity. Primed atoms are related to the corresponding atoms of the asymmetric unit by ($-x$, $-y+1$, $-z+1$).

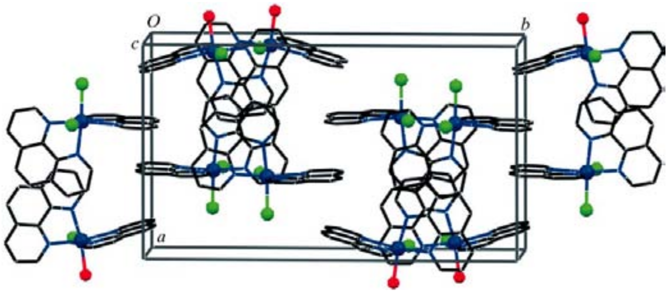


Figure 4
A projection of the crystal structure approximately down the *c* axis, showing the stacking of the aromatic residues along two perpendicular directions *a* and *c*. The solvent water molecules, chloride anions and H atoms have been omitted.

stacking, but also in the presence of other supramolecular interactions, such as hydrogen bonding, thus providing a reliable synthon for supramolecular design of new materials. Similar stacking features characterize the crystal structure of (II) (Zhao *et al.*, 2003).

Experimental

Cobalt chloride hexahydrate and 1,10-phenanthroline (phen) were supplied by Aldrich and used without further purification. All solvents used were of AR grade. For the preparation of (I), $CoCl_2\cdot6H_2O$ (0.0020 g), pyridine hydrochloride (0.0064 g) and phen (0.0037 g) were dissolved in *ca* 5 ml of EtOH by gentle heating and continuous stirring for 1 h. The solution was then allowed to stand sealed with perforated parafilm under ambient conditions. After three weeks, several dark-green blocks suitable for X-ray diffraction were observed alongside the pink prisms of (II) (see below). FT–IR: 738 (*s*), 876 (*s*), 1396 (*s*), 1456 (*m*), 1609 (*m*), 3020 (*w*), 3340 (*b*). For the preparation of (II), isonicotinic acid (0.056 g) and phen (0.0035 g) were dissolved in 5 ml of EtOH and crystallized as above. FT–IR: 735 (*s*), 874 (*s*), 1395 (*w*), 1453 (*w*), 1604 (*w*), 3018 (*w*), 3339 (*s*). For the preparation of (III), $CoCl_2\cdot6H_2O$ (0.162 g) and phen (0.242 g) were dissolved in 1 *M* HCl and heated under solvothermal conditions for a total of 177 h (24 h at 423 K peak). Maroon cubic crystals were found in the reaction vessel at the end of this period. FT–IR: 737 (*s*), 875 (*m*), 1398 (*s*), 1456 (*m*), 1604 (*m*), 3021 (*w*), 3334 (*vs*). Addition of an excess of ammonium chloride improved the quality of the crystals.

Crystal data

$[CoCl(C_{12}H_8N_2)_2(H_2O)]Cl\cdot$-
$[CoCl_2(C_{12}H_8N_2)_2]\cdot6H_2O$
$M_r = 1106.59$
Monoclinic, $P2_1/c$
$a = 14.0905\ (2)$ Å
$b = 23.9088\ (3)$ Å
$c = 14.2504\ (2)$ Å
$\beta = 98.7921\ (7)^\circ$
$V = 4744.36\ (11)$ Å^3
$Z = 4$
Mo *Kα* radiation
$\mu = 0.99$ mm^{-1}
$T = 110\ (2)$ K
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.791$, $T_{\max} = 0.827$
33988 measured reflections
11176 independent reflections
6868 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.179$
$S = 1.02$
11176 reflections
641 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -1.14$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O61—H61*A*···Cl30$^{\rm i}$	0.91	2.17	3.080 (3)	180
O61—H61*B*···O67$^{\rm ii}$	0.90	1.77	2.670 (7)	178
O63—H63*A*···Cl29	0.91	2.19	3.102 (4)	178
O63—H63*B*···O64	0.93	1.81	2.737 (6)	180
O64—H64*A*···O69	0.93	2.13	3.055 (9)	178
O64—H64*A*···Cl71	0.93	2.05	2.973 (4)	178
O64—H64*B*···O68	0.91	1.90	2.816 (10)	175
O64—H64*B*···Cl70	0.91	2.12	3.032 (4)	178
O65—H65*A*···O69	0.88	2.12	2.959 (11)	159
O65—H65*A*···Cl71	0.88	2.21	3.035 (4)	156
O65—H65*B*···O68	0.95	2.01	2.939 (8)	166
O65—H65*B*···Cl70	0.95	2.08	3.028 (4)	175
O66—H66*A*···Cl60$^{\rm ii}$	0.92	2.30	3.217 (5)	178
O66—H66*B*···O69	0.92	2.02	2.943 (11)	177
O66—H66*B*···Cl71	0.92	1.92	2.845 (6)	178

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

The asymmetric unit contains one molecule of each Co complex species and six molecules of water. The isolated chloride anion is disordered between two equally populated positions (Cl70 and Cl71). Another water molecule is disordered between the same two sites (O68 and O69) in an alternating manner with the chloride anions. The actual water content was assessed by best fit of the structural model to the diffraction data. It is consistent with the results of thermal gravimetric measurements, though the latter indicate a slightly higher content of seven water molecules (the additional molecule may represent some solvent absorbed on the crystal surface). H atoms bound to C atoms were located in calculated positions and were constrained to ride on their parent atoms, with C—H distances of 0.95 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). Those bound to O atoms were located in fixed calculated positions at O—H distances within 0.88–0.95 Å, so as to optimize the hydrogen-bonding pattern in the crystal structure. They were also assigned $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(O). H atoms of the disordered water molecule at O67, O68 and O69 were not included in the structural model but were included in the structural formula, density and *F*(000) calculations. Water molecules O66 and O67 exhibit large-amplitude displacement parameters, a possible indication of their partial disorder as well.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3176). Services for accessing these data are described at the back of the journal.

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