

Transformations of the chameleon ligand 1,10-phenanthroline-5,6-dione/diol: *cis*-dichlorido(1,10-phenanthroline-5,6-dione- κ^2N,N')-*trans*-dipyridinecobalt(II) pyridine disolvate prepared from the diol

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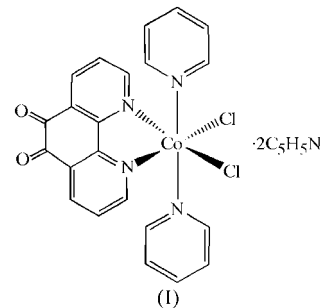
The title compound, $[\text{CoCl}_2(\text{C}_5\text{H}_5\text{N})_2(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2)] \cdot 2\text{C}_5\text{H}_5\text{N}$, is a neutral Co^{II} complex with two chloride anions coordinated in a *cis* fashion, two pyridine ligands in *trans* positions and a chelating 1,10-phenanthroline-5,6-dione ligand that completes the octahedral coordination geometry. Two pyridine solvent molecules reside in channels (about $7 \times 4 \text{ \AA}$ wide; the closest atom–atom distance within the channel is 10 \AA). The three-dimensional structure supporting these channels is held together by $\text{C} \cdots \text{H} \cdots \text{Cl}$ [$3.466(8)$ – $3.670(9) \text{ \AA}$] and $\text{C} \cdots \text{H} \cdots \text{O}$ [$3.014(9)$ – $3.285(8) \text{ \AA}$] hydrogen bonds, and can be viewed as a CsCl or bcu (body-centred cubic) net.

Comment

The 1,10-phenanthroline-5,6-dione ligand continues to be important in coordination chemistry (Calderazzo *et al.*, 2002; Fujihara *et al.*, 2003; Margiotta *et al.*, 2004; Zhang *et al.*, 2003), analytical chemistry (del Pozo *et al.*, 2005; Gatti *et al.*, 2004; Shabir & Forrow, 2003) and biophysical chemistry (Berger *et al.*, 2004; Wu *et al.*, 2002). The fate of complexes with this ligand in different solutions is therefore an important issue, and we recently showed how seemingly stable tris(phenanthroline-5,6-dione)- Co^{III} complexes could yield both Co^{II} complexes and phenanthroline-5,6-diol complexes over time (Larsson & Öhrström, 2004). This is not the only type of transformation that can occur (Fig. 1), and notably we also detected the complete transformation of the original complex to the dihydrated form (Lei & Anson, 1995; Lei *et al.*, 1996) in an aqueous solution [see (1c) in Fig. 1].

It is therefore prudent to double check any assignment of the (5,6)-carbon–carbon bond, and the carbon–oxygen bond,

in either ones own X-ray structures or structures downloaded from the Cambridge Structural Database (CSD; Allen &



Motherwell, 2002) or other sources. This is especially important for room-temperature data since subtle differences in bond lengths are all the evidence that there will be to detect the differences between the dione and the diol in the absence of an unambiguous location of the H atoms in the electron-density map. In Fig. 2, the C–O distances are plotted against the C–C distances for diketone and diol fragments found in the CSD (Version 1.7) having different bond assignments. Clearly, the large majority of data are unambiguous, but there are also a few cases that, based on these data alone, seem questionable. It can be noted that data in the small grouping at the centre of the graph correspond mainly to semiquinone radical systems.

We report here another example of an unexpected transformation, this time from the diol to the dione. The title compound, (I), was first obtained by reacting $\text{CoCl}_2(\text{s})$ with 1,10-phenanthroline-5,6-diol in pyridine. A subsequent preparation using $\text{CoCl}_2(\text{s})$ and 1,10-phenanthroline-5,6-dione in pyridine afforded compound (I) in good yield. The dione assignment was unambiguous [$\text{C6} \cdots \text{O2} = 1.216(7) \text{ \AA}$, $\text{C5} \cdots \text{O1} = 1.217(7) \text{ \AA}$ and $\text{C5} \cdots \text{C6} = 1.526(8) \text{ \AA}$]. The $\text{O1} \cdots \text{C5} \cdots \text{C6} \cdots \text{O2}$ torsion angle of $3.406(8)$ supports this assignment.

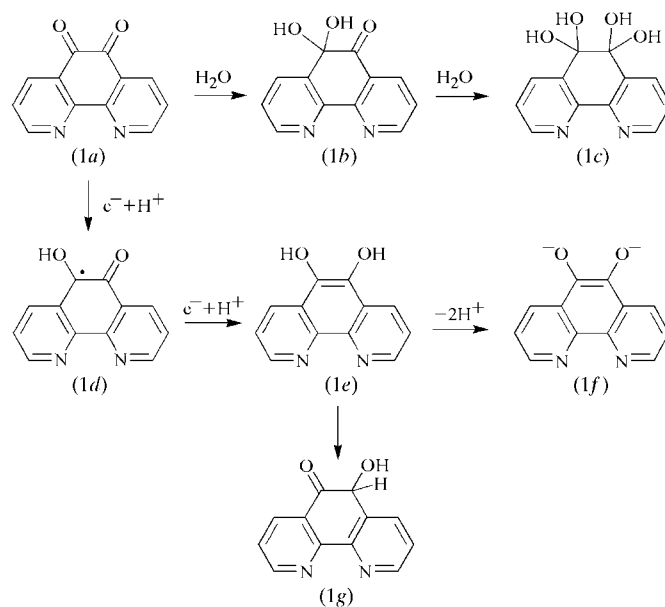


Figure 1
 Some possible transformations of the 1,10-phenanthroline-5,6-dione ligand.

The slight deviation from planarity is not unusual and is due to asymmetric interactions with a neighbouring complex, the closest O...H interactions in this case being 2.42–2.59 Å (Table 1); otherwise, the molecular structure is unremarkable (Fig. 3). All the Co–N and Co–Cl distances are as expected for a Co^{II} complex. A small deviation from linearity for the N3–Co–N4 angle [173.64 (17)°] can probably be traced to repulsion with the two chloride anions.

In contrast, the intermolecular interactions are worth a closer analysis. Despite the many aromatic molecules there are no obvious π – π interactions, but there is some indication of a σ – π interaction between the lone pairs on the N atoms and the electron-deficient part of the phenanthroline-dione ligand; the N...C distances vary between 2.65 and 2.94 Å. These interactions will, however, be weak and consequently the non-classical hydrogen bonds between ketones or coordinated chlorides and aromatic CH hydrogens reported in Table 1 may dominate among the intermolecular forces. These interactions are in agreement with other, recently published, studies on $MCl_2(L)$ complexes, where the C–H...Cl interactions were inferred to be as crucial for the resulting structure (Balasubramanian *et al.*, 2004; Xuan *et al.*, 2003).

Consequently, taking the C–H...Cl and C–H...O interactions as defining the three-dimensional connectivity, it has a distorted CsCl-type net or, according to the nomenclature described by O’Keeffe & Yaghi (2005) [see also Öhrström & Larsson (2005)], a bcu (body centred cubic) arrangement. A previous example of this type of net was found for the coordination polymer [La(2,2’-bipyridine *N,N'*-dioxide)₄](CF₃SO₃)₃·4.2MeOH (Long *et al.*, 2001). In the relatively spacious channels thus formed, the pyridine molecules cocrystallize with the complex (Fig. 4). These solvent molecules occupy 38% of the unit-cell volume, as calculated using PLATON (Spek, 2003).

From the average values of the principal mean-square atomic displacement U factors of the C atoms, it can be deduced that the pyridine solvent molecules are more flexible than the coordinated pyridine ligands, as the mean U factors are larger by 40%. The low ‘solvent’ U_{eq} value for atom N5 may also indicate disorder of the pyridine solvent molecules.

In conclusion, although (I) cannot be claimed as being porous, or having other interesting properties associated with three-dimensional nets, this study underlines the utility of network analysis (Öhrström & Larsson, 2005) for the understanding of ‘small molecule’ crystal structures.

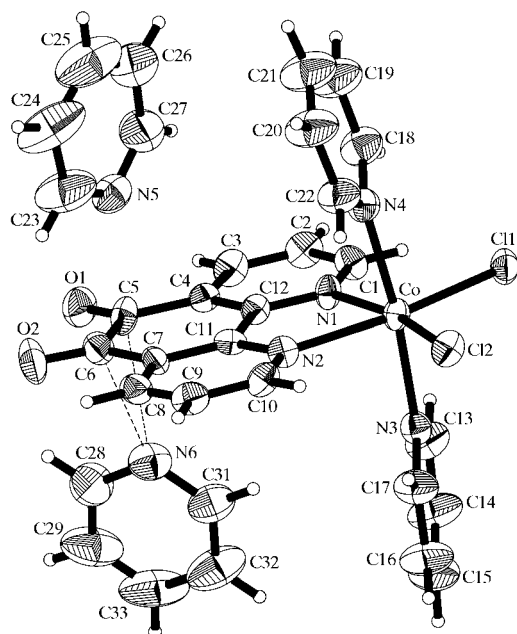


Figure 3
The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level.

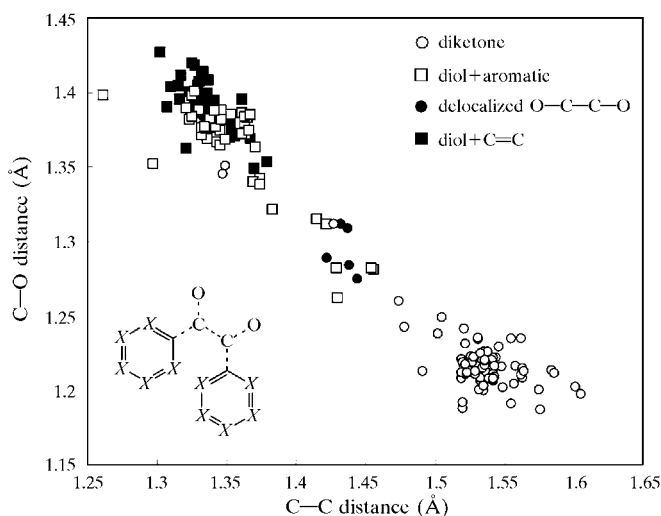


Figure 2
C–O distances versus C–C distances for diketone and diol fragments found in the CSD having different bond assignments. X is any non-metal. In all runs of the CONQUEST software (Version 1.7; Bruno *et al.*, 2002), the compounds were restricted to those having R values less than 10% and being error and disorder free; a total of 186 fragments was found.

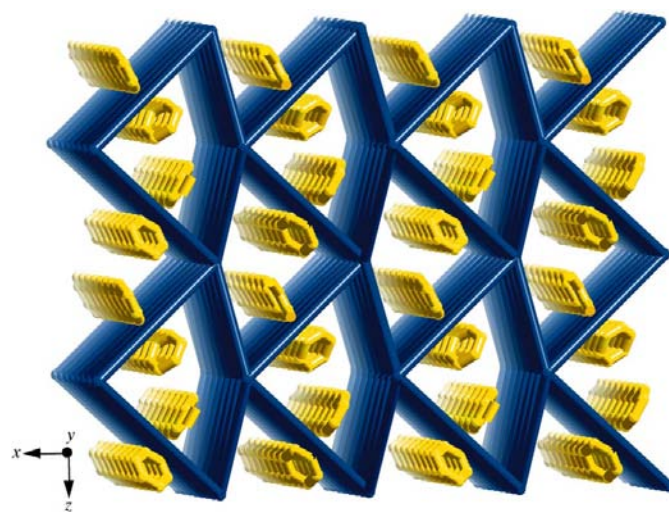


Figure 4
A view of the network structure of compound (I), including the pyridine solvent molecules. The nodes are Co atoms and the links are defined by C–H...Cl and C–H...O hydrogen bonds, giving a bcu or CsCl-type net.

Experimental

1,10-Phenanthroline-5,6-diol (Wu *et al.*, 2002) was prepared from 1,10-phenanthroline-5,6-dione (Yamada *et al.*, 1992). The latter was prepared from 1,10-phenanthroline (Aldrich). Literature procedures were used in both cases, and the identity of the diol was confirmed by its physical characteristics (colour and solubility), as well as by IR and NMR measurements. Compound (I) was first obtained by reacting CoCl₂(s) with 1,10-phenanthroline-5,6-diol in pyridine, and crystals suitable for X-ray analysis were selected directly from the product of this reaction. In a subsequent more controlled reaction, compound (I) was prepared by the reaction of CoCl₂·6H₂O (12 mg, 0.05 mmol) dissolved in pyridine (1.5 ml) and 1,10-phenanthroline-5,6-dione (10 mg, 0.05 mmol) dissolved in pyridine (4.5 ml). The solutions were mixed at room temperature, giving a deep-orange solution; after 1 h, orange uniform cubic crystals started to appear. These were filtered off and washed twice with pyridine (1.5 ml) and twice with dichloromethane (3 ml) (yield 21 mg, 69%). The identity of the crystals was confirmed by single-crystal X-ray diffraction analysis.

Crystal data

[CoCl₂(C₅H₅N)₂(C₁₂H₆-N₂O₂)]·2C₅H₅N
M_r = 656.44
 Orthorhombic, *Pna*2₁
a = 20.3809 (8) Å
b = 9.5957 (3) Å
c = 15.7370 (6) Å

V = 3077.67 (19) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.77 mm⁻¹
T = 293 (2) K
 0.1 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer 4843 independent reflections
 5614 measured reflections 3663 reflections with *I* > 2σ(*I*)

Refinement

R[*F*² > 2σ(*F*²)] = 0.051
wR(*F*²) = 0.127
S = 0.90
 4843 reflections
 389 parameters
 H-atom parameters constrained

$\Delta\rho_{\max}$ = 0.40 e Å⁻³
 $\Delta\rho_{\min}$ = -0.39 e Å⁻³
 Absolute structure: Flack (1983),
 2112 Friedel pairs
 Flack parameter: 0.56 (2)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C9—H5...Cl1 ⁱ	0.93	2.81	3.642 (7)	149
C20—H14...Cl1 ⁱⁱ	0.93	2.82	3.466 (8)	127
C8—H4...Cl2 ⁱ	0.93	2.73	3.588 (6)	154
C30—H19...Cl2 ⁱⁱⁱ	0.93	2.77	3.670 (9)	162
C14—H8...O1 ^{iv}	0.93	2.59	3.115 (9)	116
C15—H9...O1 ^{iv}	0.93	2.42	3.014 (9)	122
C2—H2...O2 ^v	0.93	2.56	3.285 (8)	135

Symmetry codes: (i) -*x* + 1, -*y* + 1, *z* - ½; (ii) -*x* + 1, -*y* + 2, *z* - ½; (iii) -*x* + ½, *y* + ½, *z* + ½; (iv) -*x* + ½, *y* - ½, *z* + ½; (v) -*x* + ½, *y* + ½, *z* + ½.

Crystals of (I) are racemically twinned with a twin scale factor (Flack parameter) of 0.56 (3). H atoms were included in calculated positions and refined as riding atoms [C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduc-

tion: DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CrystalMaker (CrystalMaker, 2006); software used to prepare material for publication: WinGX (Farrugia, 1999).

X-ray data were collected at the University of Lyon and at the University of Göteborg. We thank Professor Dominique Luneau and Professor Mikael Håkansson for help with the data collections. CD thanks the French Ministry of Research for a Lavoisier stipend.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3002). Services for accessing these data are described at the back of the journal.

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