Thiodiacetate and Oxydiacetate Cobalt Complexes: Synthesis, Structure and Stereochemical Features

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A series of cobalt complexes containing the dianionic ligands $X(CH_2COO)_2^{2-}$ (X = S, tda; or X = O, oda) is reported. The complexes [Co(tda)(bipy)(H$_2$O)]·4H$_2$O (**2**), which was characterised by X-ray crystallography, [Co(tda)(phen)(H$_2$O)] (**3**), [Co(tda){(MeO)$_2$bipy}(H$_2$O)]·2H$_2$O (**4**) and [Co(tda)(dpp)(H$_2$O)]·2H$_2$O (**5**) are obtained by reaction of the precursor complex [Co(tda)(H$_2$O)]$_n$ (**1a**) with the bidentate N-donor ligands 2,2′-bipyridine (bipy), *o*-phenanthroline (phen), 4,4′-dimethoxy-2,2′-bipyridine [(MeO)$_2$bipy] and 2,3-bis(2-pyridyl)pyrazine (dpp), respectively. The reaction of **1a** with di(2-pyridyl) ketone unexpectedly displaces tda from the coordination sphere and leads to the Co^{III} species [Co{OC(OH)-(2-pyridyl)$_2$}$_2$]$^+$[Htda]$^-$·3H$_2$O (**6**), as confirmed by an X-ray analysis. Three new oxydiacetate complexes of cobalt are also synthesised by treating the known complex [{Co(oda)-(H$_2$O)$_2$}$_2$·H$_2$O]$_n$ with 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*Bu$_2$bipy), 2,3-bis(2-pyridyl)pyrazine (dpp) and 4,4′-bipyridine (4,4′-bipy). The complexes [Co(oda)(*t*Bu$_2$bipy)(H$_2$O)]·1.5H$_2$O (**7**), [Co(oda)(dpp)(H$_2$O)]·2H$_2$O (**8**) and [{Co(oda)(H$_2$O)$_2$}$_2$(μ-4,4′-bipy)]·2H$_2$O (**9**) are structurally characterised (**8** as a methanol solvate). Complex **9** is binuclear, in contrast to **7** and **8** (mononuclear), and magnetic susceptibility measurements down to 2 K for this complex show high-spin non-correlated Co^{II} ions with a typical Curie–Weiss behaviour. The Co(oda) fragment in **7**–**9** adopts a planar (*mer*) rather than a folded (*fac*) conformation, the latter of which is common to all the M(tda) complexes but is only occasionally observed in the M(oda) ones. In the final section of the paper, the key geometric parameters that control the stereochemistry of the two ligands are determined from a statistical analysis based on the structurally characterised Co(oda) and Co(tda) complexes.

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Introduction

The thiodiacetate (tda) and oxydiacetate (oda) dianions $X(CH_2COO)_2^{2-}$ (X = S and O, respectively) are versatile ligands that have been widely explored as multidentate and chelating units for one or more metals of a different nature. They contain five atoms that are potential donors, four of which come from two carboxylate groups and one from the thioether or ether function. These ligands can bind a single metal in a tridentate manner, with the two "exo" oxygen donor atoms of the carboxylate groups being capable of additional coordination of another metal or external electrophiles. This permits the formation of homo- and heterometallic extended solids or the formation of stabilizing hydrogen bonds.

The chemistry of thiodiacetate transition metal complexes is comparatively less developed than that of the related oxydiacetate complexes. As a matter of fact, the number of X-ray characterised metal derivatives is smaller for tda than for oda derivatives (160 and 55 hits for the $O(CH_2COO)_2^{2-}$ and $S(CH_2COO)_2^{2-}$ fragments, respectively[1]). Due to our interest in this area of chemistry,[2,3] we started to explore the behaviour of thiodiacetate toward cobalt as no structure of tda-Co complexes had been reported and there were only references in the literature to the solution behaviour of tda-Co^{II} species.[4] The first structural characterisation of a tda-Co^{II} complex was simultaneously presented by us[5] and by Zhu and co-workers[6] (complex [Co(tda)(phen)(H$_2$O)]). Some additional examples, namely [Co(tda)(N-N)(H$_2$O)]·2H$_2$O and [Co(tda)(N)$_3$]·2H$_2$O, where N and N-N are nitrogen ligands, were published soon afterwards by Xu and co-workers.[7]

In this paper we present a complete report of our studies together with the synthesis and properties of new cobalt

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oxydiacetate complexes. The general coordination capabilities of both the tda and oda ligands are compared, with particular emphasis on the structural data now available for cobalt.

Results and Discussion

Cobalt Thiodiacetate Complexes

Treatment of aqueous solutions of cobalt dichloride with a 1:1 mixture of Na_2CO_3 and thiodiacetic acid, $S(CH_2COOH)_2$, affords, after the appropriate work up, dark pink block-shaped microcrystals of the complex $[Co(tda)(H_2O)]_n$ (**1a**) in good yields. Closely related thiodiacetate complexes of manganese and zinc, $[M(tda)(H_2O)]_n$, could also be synthesised by this route.[3] Complex **1a** is air-stable and soluble in water but not in solvents of low polarity. Its IR spectrum displays a very strong and broad absorption band at about 1589 cm^{-1}, which corresponds to the antisymmetric vibrations of the tda carboxylate groups. Another strong band at 1399 cm^{-1} is assigned to the corresponding symmetric vibrations.[8] The IR spectrum is identical to that of the structurally characterised polymeric complexes $[Cd(tda)(H_2O)]_n$[9] and $[Zn(tda)(H_2O)]_n$[3c,10] and, consequently, we proposed a similar crystalline structure for **1a**. During the preparation of **1a**, some dark-pink, needle-shaped crystals were also occasionally observed. The IR spectrum of this second compound, **1b**, shows only minor differences with respect that of **1a**, mainly in the region of coordinated water (see Supporting Information). This spectrum is identical to that of the already reported[11] complex $[Ni(tda)(H_2O)_3]$, therefore taking into account the analytical data, the formula of **1b** is suggested to be $[Co(tda)(H_2O)_3]$.

Complex $[Co(tda)(H_2O)]_n$ (**1a**) exists as $[Co(tda)(H_2O)_3]$ (that is **1b**) in aqueous solution. Two coordinated water molecules can easily be displaced from this species upon reaction with several bidentate N-donor ligands (see Scheme 1). In fact, aqueous solutions of **1a** react with 2,2′-bipyridine (bipy), o-phenanthroline (phen), 4,4′-dimethoxy-

2,2′-bipyridine [(MeO)$_2$bipy] and 2,3-bis(2-pyridyl)pyrazine (dpp) to give new complexes of general formula $[Co(tda)(N-N)(H_2O)]$ (N-N = bidentate N-donor ligand). These complexes can be isolated in good yields as crystalline solids containing a variable number of water molecules of hydration {namely, $[Co(tda)(bipy)(H_2O)]\cdot4H_2O$ (**2**), $[Co(tda)(phen)(H_2O)]$ (**3**), $[Co(tda)\{(MeO)_2bipy\}(H_2O)]\cdot2H_2O$ (**4**) and $[Co(tda)(dpp)(H_2O)]\cdot2H_2O$ (**5**)}. All complexes are soluble in water (but not in low polarity solvents) and are air-stable both in solution and in the solid state. Their IR spectra are characterised, besides the absorptions due to the N-donor co-ligands, by two broad absorptions corresponding to the tda carboxylate groups (for instance at 1599 and 1400 cm^{-1} for **2**). The measured effective magnetic moments (in the solid state and at room temperature) are typical of high-spin mononuclear d^7-cobalt complexes (4.3–4.9 μ_B).[12]

The crystal structures of complexes $[Co(tda)(bipy)(H_2O)]\cdot4H_2O$ (**2**) and $[Co(tda)(phen)(H_2O)]$ (**3**) were determined by X-ray diffraction methods. The structure of the latter was published while our work was in progress,[6] therefore some of its features are illustrated here but considered only for comparative purposes (see below). As for complex **2**, the coordination polyhedron around the cobalt atom is a distorted octahedron in which the metal atom is coordinated by the tridentate tda ligand in a typical *fac* arrangement. The coordination sphere is completed by the bidentate bipy ligand and one water molecule, which is bound *trans* to the sulfur donor atom of tda (Figure 1). Complex **2** is isomorphous with the known nickel,[11a] zinc[13] and copper analogues.[14] Selected bond lengths and angles of **2** are collected in Table 1.

Although coordinatively similar (also in terms of Co–O, Co–S and Co–N bond lengths), the pseudo-octahedral complexes **2** and **3** differ in two main aspects: the former features four hydration molecules while the latter has none, and the relative orientation of the N-donor group with respect to the tda ligand is different (Scheme 1). In spite of the similar coordination properties of the bipy and phen bidentate ligands, bipy lies coplanar with the coordinated oxygen donors of tda in **2** (the water ligand lies *trans* to the
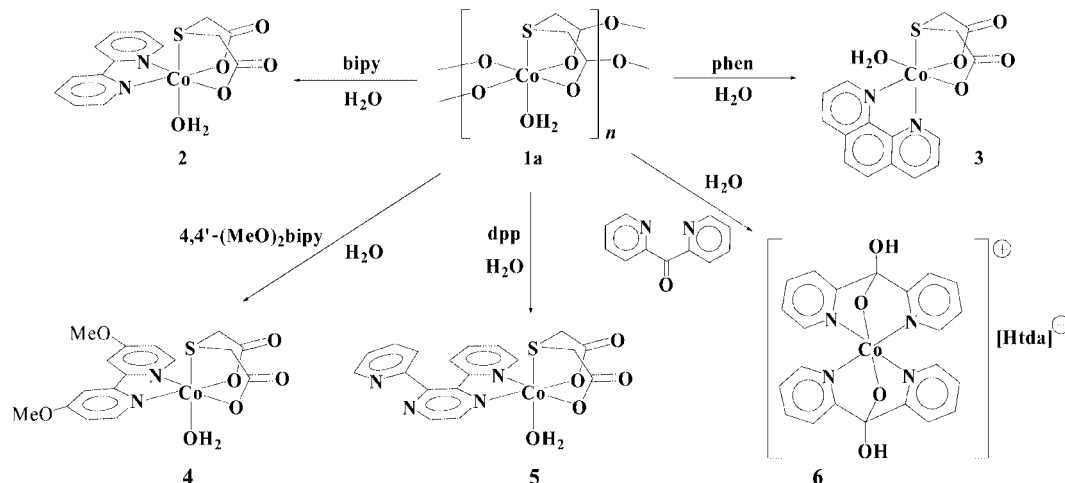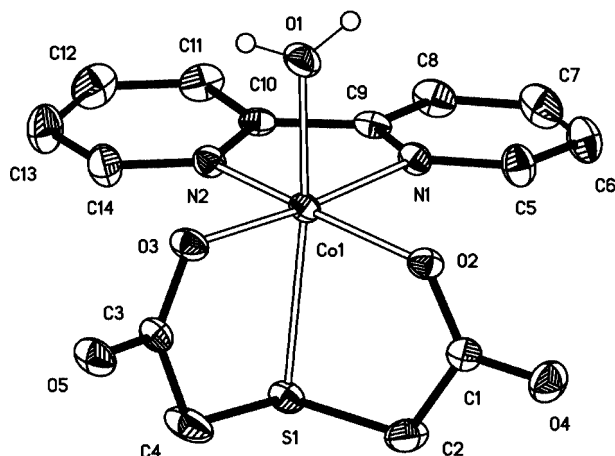

Scheme 1.

Figure 1. Molecular structure of $[Co(tda)(bipy)(H_2O)]\cdot 4H_2O$ (**2**). The hydrogen atoms, except those of the water ligand, and the crystallisation water molecules are not shown.

Table 1. Selected bond lengths [Å] and angles [°] for **2**.

Co(1)–O(3)	2.0289(15)	S(1)–C(4)	1.796(3)
Co(1)–O(2)	2.0456(15)	O(2)–C(1)	1.270(3)
Co(1)–O(1)	2.0911(17)	O(3)–C(3)	1.254(3)
Co(1)–S(1)	2.5077(10)	O(4)–C(1)	1.229(3)
Co(1)–N(2)	2.1100(19)	O(5)–C(3)	1.242(3)
Co(1)–N(1)	2.1549(18)	C(1)–C(2)	1.516(3)
S(1)–C(2)	1.791(3)	C(3)–C(4)	1.518(4)
O(3)–Co(1)–O(2)	96.56(7)	N(2)–Co(1)–N(1)	76.36(7)
O(3)–Co(1)–O(1)	85.78(7)	O(3)–Co(1)–S(1)	81.83(5)
O(2)–Co(1)–O(1)	95.44(7)	O(2)–Co(1)–S(1)	82.02(5)
O(3)–Co(1)–N(2)	97.83(7)	O(1)–Co(1)–S(1)	166.96(5)
O(2)–Co(1)–N(2)	163.56(7)	N(2)–Co(1)–S(1)	92.18(6)
O(1)–Co(1)–N(2)	93.51(8)	N(1)–Co(1)–S(1)	100.33(5)
O(3)–Co(1)–N(1)	173.82(7)	C(2)–S(1)–C(4)	104.07(18)
O(2)–Co(1)–N(1)	89.49(7)	C(2)–S(1)–Co(1)	94.86(9)
O(1)–Co(1)–N(1)	92.41(7)		

sulfur atom), although the same does not apply to phen, which adopts an upright position in **3**. In other words, it lies coplanar with the S atom while the coordinated water molecule is *trans* to one tda oxygen donor. This situation is similar to that found for the Zn-tda system, for which the bipy[13] and phen[3c] derivatives show different structures.

The crystalline solids **4** and **5** were characterised by analytical and spectroscopic methods as $[Co(tda)\{(MeO)_2\text{-}bipy\}(H_2O)]\cdot 2H_2O$ and $[Co(tda)(dpp)(H_2O)]\cdot 2H_2O$, respectively. The potentially tridentate dpp ligand coordinates in a bidentate fashion in **5**. This also occurs in the oxydiacetate derivative **8**, which has been structurally characterised (see below). The correct structure of **4** and **5** cannot be safely anticipated, however, because two isomers are also possible in this case. Their energies should be rather similar and the

adoption of a specific geometry may be caused by subtle factors. For example, the presence or absence of water of crystallisation can clearly affect the final crystal structure since hydrogen bonding is a key feature in oxydiacetate and thiodiacetate metal complexes. Coordinated and solvent water molecules fix the crystal packing of most of these derivatives by interacting with the coordinated or uncoordinated oxygen atoms of tda or oda. In actual fact, complex **2** features a 3D network of hydrogen bonding between the water ligand O1, the water solvent molecules and some oxygen atoms of the carboxylate groups of tda ligand (see Figure S2 in the Supporting Information). Consequently, we propose similar structures for **4** and **5** to that observed for **2** (Scheme 1).

An attempt to obtain an additional cobalt complex with tda was made by treating **1a** with the ligand di(2-pyridyl) ketone. The deep-red crystals obtained after the appropriate work-up have properties that are different to those observed for complexes **2**–**6**. Thus, their diamagnetism suggests the presence of a Co^III centre and their analytical data are consistent with a 1:1:2 Co:tda:di(2-pyridyl) ketone ratio. An X-ray structure determination (Figure 2) indicated that the tda ligand is protonated not coordinated, in other words it acts as a counterion. Thus, the species has the unexpected stoichiometry $[Co\{OC(OH)(2\text{-pyridyl})_2\}_2]^+[Htda]^-\cdot 3H_2O$ (**6**). Essentially, two di(2-pyridyl) ketone molecules have been hydrolysed and deprotonated in a process that has already been described (Scheme 2).[15] The latter molecules act as two staggered tridentate *fac* ligands that confer a pseudo-octahedral geometry to the oxidized Co^III centre. Selected bond lengths and angles of **6** are collected in Table 2. The
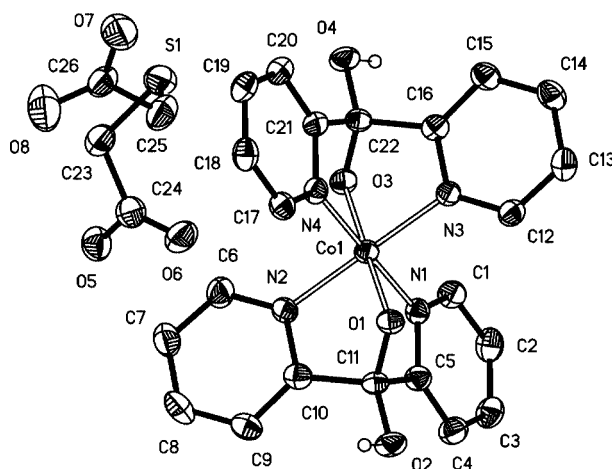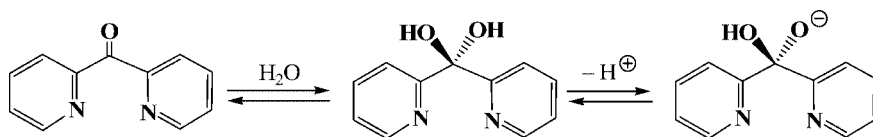

Figure 2. Crystal structure of $[Co\{OC(OH)(2\text{-pyridyl})_2\}_2]^+$-$[Htda]^-\cdot 3H_2O$ (**6**). Solvent water molecules are not shown.

Scheme 2.

cationic part of **6**, [Co{OC(OH)(2-pyridyl)$_2$}$_2$]$^+$, has been previously characterised for other cobalt complexes with different counterions.[16] There is good structural consistency among the latter, so their geometrical features do no require further comment.
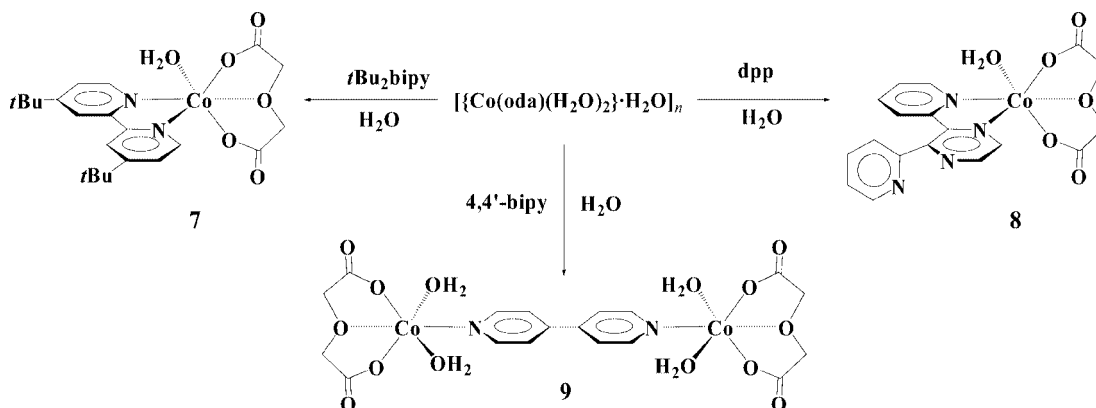
Table 2. Selected bond lengths [Å] and angles [°] for **6**.

Co(1)–O(1)	1.886(3)	O(3)–C(22)	1.395(7)
Co(1)–O(3)	1.886(3)	O(1)–C(11)	1.404(7)
Co(1)–N(1)	1.913(4)	O(2)–C(11)	1.382(6)
Co(1)–N(4)	1.922(4)	O(4)–C(22)	1.376(6)
Co(1)–N(3)	1.926(4)	O(5)–C(24)	1.293(8)
Co(1)–N(2)	1.932(4)	O(6)–C(24)	1.217(8)
S(1)–C(23)	1.794(7)	O(7)–C(26)	1.227(8)
S(1)–C(25)	1.816(8)	O(8)–C(26)	1.221(9)
O(1)–Co(1)–O(3)	179.48(16)	N(1)–Co(1)–N(3)	91.24(18)
O(1)–Co(1)–N(1)	82.90(17)	N(4)–Co(1)–N(3)	88.31(18)
O(3)–Co(1)–N(1)	96.70(17)	O(1)–Co(1)–N(2)	82.81(17)
O(1)–Co(1)–N(4)	97.67(17)	O(3)–Co(1)–N(2)	97.51(17)
O(3)–Co(1)–N(4)	82.73(17)	N(1)–Co(1)–N(2)	88.99(18)
N(1)–Co(1)–N(4)	179.32(17)	N(4)–Co(1)–N(2)	91.46(19)
O(1)–Co(1)–N(3)	96.53(17)	N(3)–Co(1)–N(2)	179.27(16)
O(3)–Co(1)–N(3)	83.15(17)	C(23)–S(1)–C(25)	101.8(3)

Cobalt Oxydiacetate Compounds

The number of structurally characterised cobalt oxydiacetate complexes has grown considerably in the last few years. Some crystallographic reports of Co-oda complexes have appeared,[17] and it is worth mentioning, in particular, that the structure of complex [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$[18] has been re-determined twice.[19] Additionally, Jiang and Wang have pointed out a topological isomerism between this complex and [{Co(oda)(H$_2$O)}·H$_2$O]$_n$, and discussed their interconversion.[19a] Since our original report on this chemistry,[2a] we have continued our studies of the chemical reactivity of [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$ and we can now describe here the synthesis and structural characterisation of three new Co-oda complexes.

The reaction of aqueous solutions of the complex [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$ with 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*Bu$_2$bipy), 2,3-bis(2-pyridyl)pyrazine (dpp) and 4,4′-bipyridine (4,4′-bipy) yields, after the appropriate work-up, crystals of [Co(oda)(*t*Bu$_2$bipy)(H$_2$O)]·1.5H$_2$O (**7**), [Co(oda)-(dpp)(H$_2$O)]·2H$_2$O (**8**) and [{Co(oda)(H$_2$O)$_2$}$_2$(μ-4,4′-bipy)]·2H$_2$O (**9**), respectively, with good yields (see Scheme 3).

These complexes are air-stable both in solution and in the solid state. They are soluble in water and complex **7** is also soluble in ethanol. The IR spectra show an intense broad absorption around 1600 cm^{-1} due to the antisymmetric vibrations of the coordinated carboxylate groups of oxydiacetate. We have shown in previous work[2a,2d] that the position of the COC stretch of the oxydiacetate ligand (a characteristic sharp and strong absorption) depends on the disposition of the ligand in the coordination sphere. Thus, when the signal appears above 1100 cm^{-1} the oda ligand adopts a planar conformation (*mer*), whereas in other cases the arrangement is non-planar. Bands above the latter limit for complexes **7**–**9** clearly indicate a planar coordination mode (*mer*), and this was validated by the X-ray analyses. Interestingly, while the known Co(oda) fragments can adopt either a *fac* or a *mer* arrangement, the M(tda) analogue is, to date, invariably *fac* for cobalt as well as for all known transition metal complexes (see below).

Complex **7** is monomeric (Figure 3), and selected structural data are reported in Table 3. The coordination geometry of the cobalt atom is distorted octahedral due to the low bite angle of oda [*transoid* O1–Co–O5 angle of 150.42(10)°].
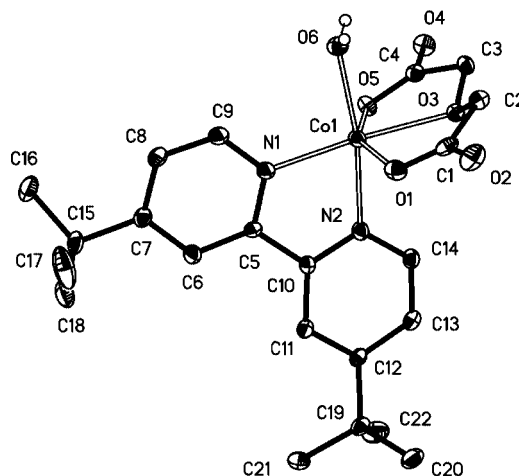
Figure 3. Drawing of one of the two independent molecules in the asymmetric unit of [Co(oda)(*t*Bu$_2$bipy)(H$_2$O)]·1.5H$_2$O (**7**). The hydrogen atoms, except those of the water ligand, and the crystallisation water molecules are not shown.

Scheme 3.

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Although the *t*Bu₂bipy ligand is common in coordination chemistry (187 hits in the Cambridge Structural Database,[1a] CSD), it appears that complex **7** is the first structure of a cobalt complex with this ligand.

Table 3. Selected bond lengths [Å] and angles [°] for **7**.

	Molecule 1		
Co(1)–O(5)	2.055(2)	O(5)–Co(1)–N(2)	87.99(10)
Co(1)–O(1)	2.056(2)	O(1)–Co(1)–N(2)	90.20(10)
Co(1)–N(1)	2.080(3)	N(1)–Co(1)–N(2)	77.04(10)
Co(1)–N(2)	2.112(3)	O(5)–Co(1)–O(6)	89.96(10)
Co(1)–O(6)	2.120(2)	O(1)–Co(1)–O(6)	96.35(10)
Co(1)–O(3)	2.169(2)	N(1)–Co(1)–O(6)	94.50(10)
O(1)–C(1)	1.262(4)	N(2)–Co(1)–O(6)	170.05(10)
O(2)–C(1)	1.242(4)	O(5)–Co(1)–O(3)	76.40(8)
O(3)–C(2)	1.429(4)	O(1)–Co(1)–O(3)	74.95(9)
O(3)–C(3)	1.439(4)	N(1)–Co(1)–O(3)	173.57(10)
O(4)–C(4)	1.245(4)	N(2)–Co(1)–O(3)	100.75(9)
O(5)–C(4)	1.265(4)	O(6)–Co(1)–O(3)	88.21(9)
C(1)–C(2)	1.535(5)	C(2)–O(3)–C(3)	116.8(2)
C(3)–C(4)	1.533(4)	O(2)–C(1)–O(1)	125.0(4)
O(5)–Co(1)–O(1)	150.42(10)	O(2)–C(1)–C(2)	118.1(3)
O(5)–Co(1)–N(1)	109.39(10)	O(4)–C(4)–O(5)	124.9(3)
O(1)–Co(1)–N(1)	98.92(11)		
	Molecule 2		
Co(2)–O(11)	2.070(2)	N(3)–Co(2)–O(12)	94.06(10)
Co(2)–N(3)	2.082(2)	O(11)–Co(2)–O(7)	150.95(9)
Co(2)–O(12)	2.090(2)	N(3)–Co(2)–O(7)	106.58(10)
Co(2)–O(7)	2.103(2)	O(12)–Co(2)–O(7)	90.34(9)
Co(2)–N(4)	2.108(3)	O(11)–Co(2)–N(4)	94.15(10)
Co(2)–O(9)	2.113(2)	N(3)–Co(2)–N(4)	77.15(10)
O(7)–C(23)	1.256(4)	O(12)–Co(2)–N(4)	169.90(10)
O(8)–C(23)	1.251(4)	O(7)–Co(2)–N(4)	87.48(10)
O(9)–C(25)	1.420(4)	O(11)–Co(2)–O(9)	75.16(8)
O(9)–C(24)	1.423(4)	N(3)–Co(2)–O(9)	172.85(10)
O(10)–C(26)	1.249(4)	O(12)–Co(2)–O(9)	92.64(9)
O(11)–C(26)	1.253(4)	O(7)–Co(2)–O(9)	75.84(9)
C(23)–C(24)	1.529(4)	N(4)–Co(2)–O(9)	96.38(9)
C(25)–C(26)	1.535(4)	C(25)–O(9)–C(24)	117.2(2)
O(11)–Co(2)–N(3)	102.03(10)	O(8)–C(23)–O(7)	125.5(3)
O(11)–Co(2)–O(12)	92.54(9)	O(10)–C(26)–O(11)	125.7(3)

Complex **8** was obtained in the solid state as [Co-(oda)(dpp)(H₂O)]·2H₂O, although the X-ray characterisation was carried out with crystals of the methanol solvate [Co(oda)(dpp)(H₂O)]·H₂O·1/2MeOH that is formed upon recrystallisation from a MeOH/H₂O mixture. Complex **8** is also a monomer, with the cobalt atom octahedrally coordinated by three O atoms of the oda ligand in a quasi-planar arrangement, two N atoms of the 2,3-bis(2-pyridyl)pyrazine molecule and one water molecule (Figure 4). As seen in Table 4, the Co–O bonds range between 2.05 and 2.16 Å and the Co–N bonds are as long as 2.095(3) and 2.131(3) Å. Despite possessing three N donor atoms, the dpp ligand is bidentate in **8** since one of the two pyridyl substituents remains uncoordinated. There is one previous structurally characterised example of a Co-ddp complex[20] in which the dpp ligand bridges two cobalt atoms in a μ,κ²,κ² coordination mode. Interestingly, all attempts to force coordination of the N atom at the free pyridine ring failed. In fact, further reaction of complex **8** with [{Co(oda)(H₂O)₂}·H₂O]ₙ or the reaction of two equivalents of the latter starting ma-

terial with 2,3-bis(2-pyridyl)pyrazine did not produce the expected coordination. The geometry of **8** is related to that of **7** and other complexes of formula [Co(oda)(N-N)-(H₂O)],[21] therefore no further comment is necessary.
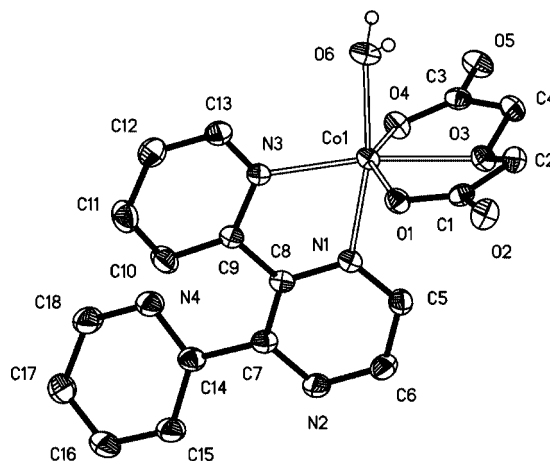

Figure 4. ORTEP drawing of **8** as the methanol solvate [Co(oda)-(dpp)(H₂O)]·H₂O·1/2MeOH. The hydrogen atoms, except those of the water ligand, and the solvent molecules are not shown.

Table 4. Selected bond lengths [Å] and angles [°] for **8**.

Co(1)–O(1)	2.077(2)	O(1)–C(1)	1.269(4)
Co(1)–O(3)	2.159(2)	O(2)–C(1)	1.230(4)
Co(1)–O(4)	2.055(2)	O(3)–C(2)	1.419(4)
Co(1)–O(6)	2.099(2)	O(3)–C(4)	1.432(4)
Co(1)–N(1)	2.131(3)	O(4)–C(3)	1.257(4)
Co(1)–N(3)	2.095(3)	O(5)–C(3)	1.245(4)
O(1)–Co(1)–O(3)	74.76(8)	N(3)–Co(1)–O(6)	93.65(10)
O(1)–Co(1)–O(6)	93.45(9)	O(4)–Co(1)–N(1)	87.13(10)
O(4)–Co(1)–O(1)	148.98(9)	N(3)–Co(1)–N(1)	76.51(10)
O(4)–Co(1)–O(3)	74.61(8)	O(6)–Co(1)–N(1)	168.69(10)
O(4)–Co(1)–O(6)	92.08(9)	N(3)–Co(1)–O(3)	169.13(9)
O(6)–Co(1)–O(3)	91.42(9)	N(1)–Co(1)–O(3)	99.23(10)
O(4)–Co(1)–N(3)	114.75(10)	O(5)–C(3)–O(4)	125.5(3)
O(1)–Co(1)–N(3)	95.33(10)	O(2)–C(1)–O(1)	126.1(3)
O(1)–Co(1)–N(1)	93.02(10)		

4,4′-Bipyridine was selected as a ligand on the basis of its capacity to afford coordination polymers.[22] However, complex **9** is a binuclear species in which the 4,4′-bipy ligand bridges two cobalt centres (Figure 5). The coordination geometry of each cobalt atom is pseudo-octahedral, with the ethereal oxygen atom of the planar oda ligand O4 occupying a *trans* position with respect to the N-donor atom N1 and the two water ligands mutually *trans*. Selected structural data are collected in Table 5. Complex **9** is isostructural with the zinc analogue [{Zn(oda)(H₂O)₂}₂(μ-4,4′-bipy)]·2H₂O.[23] Other cobalt complexes containing a tridentate dianionic ligand may be related to the present species.[24]

The magnetic characterisation of complex **9** was performed with a SQUID susceptometer in the range 1.9–300 K. Magnetisations were measured up to 6 T and showed that loose powder samples have a strong tendency to align with the imposed field, therefore measurements were re-performed with a pellet. The behaviour of both the
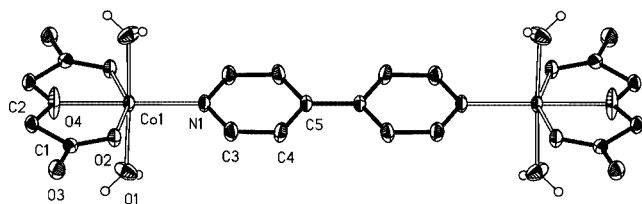
Figure 5. Molecular structure of binuclear complex [{Co(oda)(H$_2$O)$_2$}$_2$(μ-4,4′-bipy)]·2H$_2$O (**9**). The hydrogen atoms, except those of the water ligand, and the crystallisation water molecules are not shown.

Table 5. Selected bond lengths [Å] and angles [°] for **9**.

Co(1)–O(1)	2.080(3)	O(4)–C(2)	1.385(3)
Co(1)–O(2)	2.063(2)	N(1)–C(3)	1.333(3)
Co(1)–O(4)	2.067(3)	C(1)–C(2)	1.525(4)
Co(1)–N(1)	2.082(3)	C(3)–C(4)	1.371(4)
O(2)–C(1)	1.262(3)	C(4)–C(5)	1.385(4)
O(3)–C(1)	1.232(3)	C(5)–C(5)[b]	1.478(7)
O(1)–Co(1)–N(1)	91.20(8)	O(2)[a]–Co(1)–O(1)	91.11(11)
O(1)–Co(1)–O(2)	88.35(11)	O(1)[a]–Co(1)–O(1)	177.61(15)
O(1)–Co(1)–O(4)	88.80(8)	O(2)–Co(1)–N(1)	103.03(5)
O(2)–Co(1)–O(4)	76.97(5)	O(4)–Co(1)–N(1)	180.0
O(2)[a]–Co(1)–O(2)	153.94(11)	O(3)–C(1)–O(2)	124.7(3)
O(4)–Co(1)–O(1)[a]	88.80(8)		

[a] Symmetry transformations used to generate equivalent atoms: –x + 2, y, –z + 1. [b] –x + 2, –y + 1, –z + 1.

susceptibility χ_m and its product with temperature ($\chi_m T$) are typical of a paramagnetic system, as shown in Figure 6. The $\chi_m T$ value (5.15 emu K mol^{-1} at 300 K) is consistent with two nearly uncorrelated high-spin Co^{II} ions, with corresponding factors of 2.35. On lowering the temperature, $\chi_m T$ starts to decrease significantly below 60 K, while χ_m rises monotonically without reaching any maximum. A plot of the inverse susceptibility $1/\chi_m$ vs. T gives a Curie–Weiss temperature θ of +4.4 K above 50 K. High-spin Co^{II} has a $^4T_{1g}$ ground state and, with spin-orbit coupling leaving the orbital moment unquenched, large deviations of g from the free-electron value and large zero-field splittings are expected. The latter, along with possibly some weak exchange interaction between the two cobalt atoms, accounts for the observed decrease of $\chi_m T$ at lower temperatures.
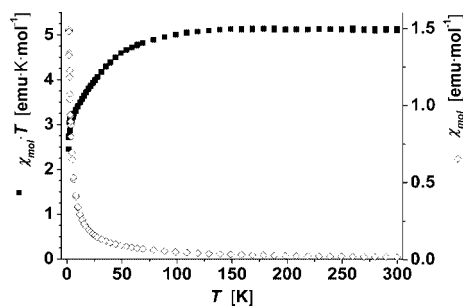

Figure 6. Molar magnetic susceptibility χ_m (✧, cgs units) and its product with temperature $\chi_m T$ (■, cgs units) of complex **9** between 1.9 and 300 K.

Factors Governing the Stereochemical Features of the tda and oda Ligands

Although we have published several contributions concerning the coordination chemistry of tda and oda,[2,3,5] this is the first paper in which we address the behaviour of both ligands toward the same metal centre. By exploiting the small but not insignificant number of CSD structures[1a] for all the known cobalt compounds,[25] we have been able to determine the structural parameters that affect the wrapping mode of both types of ligands toward cobalt.

In spite of their similar structures, the presence of a central sulfur or oxygen atom in tda and oda, respectively, has a significant effect on the bonding modes at the metal centres. To date, it has been found that when tda acts as a tridentate ligand it is invariably folded about the M–S vector (*fac* coordination), while oda can adapt to both the folded and planar (*mer*) modes (Scheme 4). We have previously determined the energy differences between the two possible oda conformations in models such as [Ni(oda)-(H$_2$O)$_3$] and [VO(oda)(H$_2$O)$_2$] by DFT calculations[2a,2d] and concluded that there is a small ΔE value between the two isomers (of the order of 2 kcal mol^{-1} for the Ni compound). Under these circumstances, intermolecular interactions, such as the hydrogen-bond networks involving water crystallisation molecules, probably determine the specific conformation of oxydiacetate.
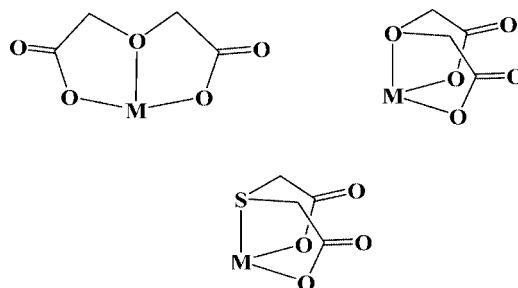
Scheme 4.

Different sets of geometric parameters are involved in the two possible coordination modes of the ligands. Among these parameters, significant variations are observed for the Co–X (X = O or S) coordination bonds, the O$_{carbox.}$–Co–O$_{carbox.}$ and Co–X–C angles at cobalt and at the heteroatom (C–X–C) and the torsion angles about the X–C and C–C bonds. Thus, it is interesting to determine which parameters exercise most control over the stereochemical features. The Co–S distances fall in the small range 2.508–2.560 Å, with a mean value of 2.52(2) Å (see Figure S3 in the Supporting Information). The corresponding Co–O distances are shorter of course, although their range is wider [2.074–2.269 Å, with a mean value of 2.13(5) Å]. In this case the data refer to both ligand conformations but, in spite of an evident overlap zone, the longer Co–O distances are associated with ligand folding. Beside the Co–X distance, the C–X–C angle is also important since its flexibility is related to the ultimate parameters of folding, in other words the O$_{carbox.}$–Co–O$_{carbox.}$ coordination angle and the

$O_{carbox.}$–Co–X–C torsion angle. The latter parameters should simultaneously approach the limiting values of 90° or 180° for the folded and planar conformations, respectively. Figure 7 shows a quasi-linear interdependence between M–X and C–X–C.
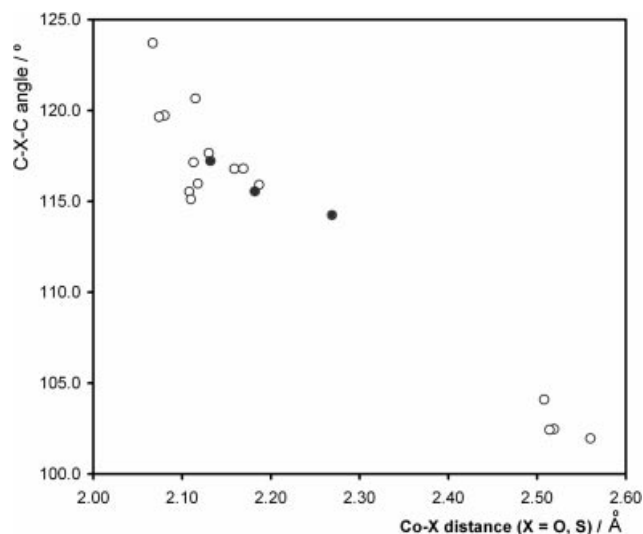
Figure 7. Plot of the Co–X distance [Å] vs. the C–X–C angle [°] showing two separate regions for oda and tda cobalt complexes (black circles are the *fac*-oda compounds).

The question remains, however, as to why the ligand tda never adopts the planar conformation. The average value for the C–O–C angle in uncoordinated ethers is higher than the corresponding C–S–C one in thioethers. Such a difference has a simple theoretical justification based on the different electronegativities of oxygen and sulfur.[26] In the cobalt complexes analysed these angles are within the range 102.0–104.1° for the tda ligand and 114.2–120.7° for the oda ligand. It is evident that ligand folding/unfolding accompanies a significant remodulation of the Co–X and C–X–C parameters, which also depend on electronic constraints (ionic radius, oxidation and spin state of the metal, electronegativity of the X atom, different hard/soft character of the X atom). According to Figure 7, a Co–S distance within the observed range or even shorter should accompany an acute C–S–C angle, which is not yet suitable for conferring the *mer* conformation to tda. This can be verified by considering the correlation diagram between the C–X–C and $O_{carbox.}$–Co–$O_{carbox.}$ angles (Figure 8), from which it becomes evident that there cannot be sufficient opening of the coordination angle at the metal centre for the C–S–C values in question. In conclusion, the planar arrangement (*mer*) is essentially unattainable for Co(tda) complexes, in fact it is impossible to build a model with tolerable distances and angles. Similar graphs to that shown in Figure 8, in which a clear separation of the three coordination modes is observed, can be obtained by plotting the Co–X–CH$_2$ angles against the $O_{carbox.}$–Co–$O_{carbox.}$ angle or against the $O_{carbox.}$–Co–X–C torsion angle (see Supporting Information).
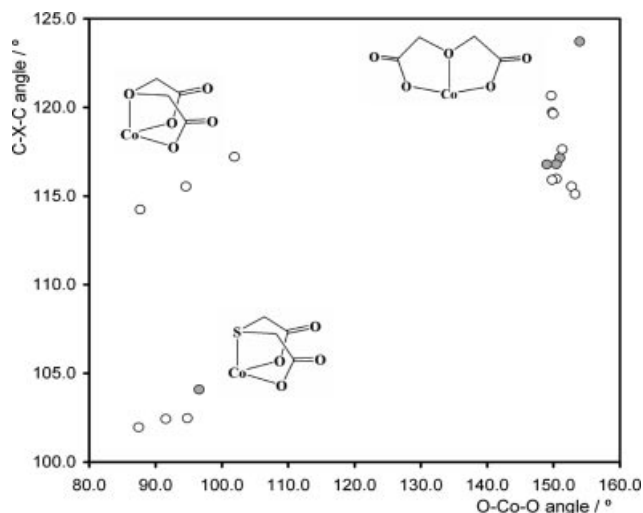
Figure 8. Plot of the C–X–C angle [°] vs. the $O_{carbox.}$–Co–$O_{carbox.}$ angle [°] (shaded circles represent the complexes reported in this paper).

Experimental Section

General: All preparations and other operations were carried out under aerobic conditions. Thiodiacetic acid, oxydiacetic acid and other chemicals were obtained from commercial sources and were used without further purification. [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$ was prepared according to the procedure previously reported by us.[2a] Microanalyses (C, H, N) were carried out by the Microanalytical Service of CITIUS. IR spectra were recorded with a Perkin–Elmer Model 883 spectrophotometer (Nujol emulsion in NaCl plates). Magnetic moments were measured in the solid state, at room temperature, with a Sherwood Scientific (Cambridge Research Laboratory) magnetic balance, and between 1.9 and 300 K with a Cryogenic S600 SQUID magnetometer. Molar susceptibilities were corrected using Pascal's constants.[27] For the pellet measurement, the measure had to be corrected for some ferromagnetic impurities. The corrected curve agreed well with a zero-field cooled measurement done on a loose powder sample prior to magnetisation measurements. No significant temperature-independent paramagnetism was found.

[Co(tda)(H$_2$O)]$_n$ (1a): Na$_2$CO$_3$ (0.63 g, 6 mmol) was added to a solution of S(CH$_2$COOH)$_2$ (0.90 g, 6 mmol) in water (20 mL). The mixture was stirred until the evolution of CO$_2$ ceased and then added to a solution of CoCl$_2$·6H$_2$O (1.42 g, 6 mmol) in water (15 mL). The resulting solution was stirred for 10 min, then acetone was added and the solution was kept at room temperature overnight. The dark pink crystals of **1a** that formed were filtered off, washed with acetone and diethyl ether and air dried (1.3 g, 96% yield). IR: $\tilde{v}$ = 3548–3087 (br), 1637 (vs), 1589 (vs), 1459 (s), 1399 (vs), 1376 (vs), 1243 (m), 1180 (w), 917 (m), 873 (w), 806 (m), 779 (s), 698 (s) cm^{-1}. C$_4$H$_6$CoO$_5$S (225.09): calcd. C 21.34, H 2.69; found C 20.86, H 3.00. Small amounts of pink needle crystals of complex [Co(tda)(H$_2$O)$_3$] (**1b**) were observed and manually separated in some of the preparations of **1a**. IR: $\tilde{v}$ = 3548 (s), 3482–3018 (br), 1635 (vs), 1585 (vs), 1406 (s), 1376 (vs), 1254 (w), 1229 (m), 1204 (w), 1178 (w), 939 (m), 865 (m), 790 (s), 763 (s), 705 (s), 663 (m) cm^{-1}. C$_4$H$_{10}$CoO$_7$S (261.12): calcd. C 18.40, H 3.86; found C 18.73, H 3.96.

[Co(tda)(bipy)(H$_2$O)]·4H$_2$O (2): Bipy (0.156 g, 1 mmol) was added to a suspension of **1a** (0.261 g, 1 mmol) in water. This mixture,

which turned deep pink, was heated with stirring until all the solid had dissolved and then concentrated. Complex **2** crystallised upon evaporation of the solvent at room temperature after a few days. The pink crystals were filtered off, washed with water, acetone and diethyl ether and air dried (0.38 g, 84% yield). IR: $\tilde{v}$ = 3660–3036 (br), 1599 (vs), 1492 (s), 1462 (s), 1442 (vs), 1400 (s), 1375 (vs), 1338 (s), 1316 (s), 1253 (m), 1233 (m), 1196 (w), 1179 (w), 1157 (w), 1102 (w), 1061 (m), 1043 (w), 1021 (m), 1011 (w), 969 (w), 932 (s), 899 (m), 875 (w), 764 (vs), 735 (s), 698 (s), 648 (s), 626 (m) cm^{-1}. μ_{eff} = 4.5 μ_B at 25 °C. $C_{14}H_{22}CoN_2O_9S$ (453.33): calcd. C 37.09, H 4.89, N 6.18; found C 37.11, H 4.69, N 6.61.

[Co(tda)(phen)(H$_2$O)] (3): A solution of *o*-phen·H$_2$O (0.198 g, 1 mmol) in 10 mL of methanol was added to a suspension of **1a** (0.230 g, 1 mmol) in 20 mL of water. This mixture, which turned deep pink immediately, was stirred and heated (90 °C) until all the solids had dissolved. It was then concentrated to a volume of about 15 mL. Slow evaporation of the solvent resulted in the formation of crystals of **3**, which were collected by filtration, washed with cold water, acetone and diethyl ether and dried in air (0.38 g, 90%). IR: $\tilde{v}$ = 3552–3088 (br), 3063 (w), 1644 (vs), 1584 (vs), 1516 (m), 1494 (w), 1426 (w), 1313 (m), 1213 (m), 1183 (w), 1136 (m), 1101 (m), 988 (w), 933 (m), 918 (m), 868 (m), 846 (s), 788 (m), 773 (m), 758 (m), 723 (s), 665 (m), 640 (m) cm^{-1}. μ_{eff} = 4.3 μ_B at 25.5 °C. $C_{16}H_{14}CoN_2O_5S$ (405.29): calcd. C 47.42, H 3.48, N 6.91; found C 46.97, H 3.38, N 6.76.

[Co(tda){(MeO)$_2$bipy}(H$_2$O)]·2H$_2$O (4): (MeO)$_2$bipy (0.108 g, 0.5 mmol) was added to a suspension of **1a** (0.120 g, 0.5 mmol) in 15 mL of water. This mixture, which turned red, was heated at 90 °C with stirring until all the solid had dissolved and was then poured into a crystallisation dish. Slow evaporation of water resulted in the formation of red crystals of **4**, which were collected by filtration, washed with acetone and diethyl ether and dried in air (0.18 g, 75% yield). IR: $\tilde{v}$ = 3669–3951 (br), 1602 (vs), 1496 (s), 1460 (s), 1451 (s), 1413 (s), 1402 (s), 1375 (s), 1339 (s), 1281 (s), 1245 (s), 1224 (s), 1186 (w), 1161 (w), 1130 (w), 1096 (w), 1038 (s), 1004 (m), 921 (m), 865 (m), 838 (s), 793 (m), 766 (m), 732 (m), 694 (m), 665 (m) cm^{-1}. $C_{26}H_{30}CoN_4O_{11}S$ (665.53): calcd. C 40.24, H 4.60, N 5.87; found C 40.24, H 4.45, N 5.95.

[Co(tda)(dpp)(H$_2$O)]·2H$_2$O (5): This complex was obtained as red crystals (0.11 g, 74% yield) following a similar synthetic procedure as described for **4** but with 2,3-bis(2-pyridyl)pyrazine (0.07 g, 0.3 mmol). IR: $\tilde{v}$ = 3601–3039 (br), 1593 (vs), 1529 (m), 1475 (s), 1452 (s), 1394 (vs), 1376 (vs), 1298 (m), 1253 (m), 1238 (m), 1215 (m), 1164 (s), 1139 (m), 1121 (m), 1099 (m), 1083 (w), 1059 (w), 1038 (s), 1021 (m), 996 (m), 969 (w), 938 (s), 920 (s), 873 (m), 819 (m), 788 (vs), 761 (s), 752 (s), 705 (s), 662 (m), 647 (m), 624 (s) cm^{-1}. $C_{18}H_{20}CoN_4O_7S$ (495.37): calcd. C 43.60, H 4.03, N 11.30; found C 43.95, H 3.90, N 11.70.

[Co{OC(OH)(2-pyridyl)$_2$}$_2$][Htda]·3H$_2$O (6): Di(2-pyridyl) ketone (0.184 g, 1 mmol) was added to a suspension of **1a** (0.13 g, 0.5 mmol) in 15 mL of water. This mixture was heated at 90 °C for 0.5 h and then filtered. Slow evaporation of the filtrate resulted in the formation of red crystals of **3**, which were collected by filtration, washed with acetone and diethyl ether and dried in air (0.25 g, 75% yield). IR: $\tilde{v}$ = 3666–3080 (br), 1589 (vs), 1443 (vs), 1403 (s), 1376 (s), 1287 (vs), 1235 (vs), 1200 (m), 1164 (s), 1130 (w), 1085 (s), 1059 (w), 1023 (s), 933 (m), 886 (w), 868 (w), 806 (s), 768 (s), 701 (s), 667 (s) cm^{-1}. $C_{26}H_{29}CoN_4O_{11}S$ (664.53): calcd. C 46.95, H 4.36, N 8.43; found C 46.83, H 4.48, N 8.33.

[Co(oda)(*t*Bu$_2$bipy)(H$_2$O)]·1.5H$_2$O (7): A solution of 4,4′-*t*Bu$_2$bipy (0.147 g, 0.5 mmol) in 10 mL of ethanol was added to a solution of [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$ (0.122 g, 0.5 mmol) in 15 mL of water.

This mixture, which turned deep pink immediately, was stirred and heated (90 °C) until all the solid had dissolved. It was then concentrated to a volume of about 15 mL. Slow evaporation of the solvent resulted in the formation of crystals of **7**, which were washed with cold water, acetone and diethyl ether and dried in air (0.20 g, 72% yield). IR: $\tilde{v}$ = 3496–3037 (br), 1613 (vs), 1547 (s), 1408 (vs), 1348 (m), 1305 (s), 1265 (w), 1250 (m), 1200 (m), 1131 (s), 1111 (s), 1038 (w), 1015 (s), 917 (s), 897 (m), 858 (s), 668 (w), 604 (s) cm^{-1}. μ_{eff} = 4.5 μ_B at 20 °C. $C_{22}H_{33}CoN_2O_{7.5}$ (504.44): calcd. C 52.37, H 6.15, N 5.55; found C 52.03, H 6.47, N 5.68.

[Co(oda)(dpp)(H$_2$O)]·2H$_2$O (8): 2,3-Bis(2-pyridyl)pyrazine (0.117 g, 0.5 mmol) was added to an aqueous solution of [{Co(oda)-(H$_2$O)$_2$}·H$_2$O]$_n$ (0.122 g, 0.5 mmol). This mixture, which turned red immediately, was stirred at 90 °C until the solid had dissolved and was then concentrated. Slow evaporation of water gave red crystals of **8**, which were collected by filtration, washed with cold water, acetone and diethyl ether and dried in air (0.15 g, 63% yield). IR: $\tilde{v}$ = 3636–32980 (br), 1605 (vs), 1436 (s), 1422 (s), 1398 (s), 1346 (m), 1305 (s), 1238 (m), 1169 (m), 1122 (s), 1096 (m), 1061 (m), 1038 (m), 1023 (s), 993 (m), 969 (w), 919 (m), 872 (m), 824 (w), 790 (s), 770 (m), 744 (m), 725 (m), 666 (w), 639 (m), 621 (m) cm^{-1}. $C_{18}H_{20}CoN_4O_8$ (479.31): calcd. C 45.07, H 4.17, N 11.68; found C 45.09, H 4.14, N 11.90. Good quality crystals of this complex were obtained by recrystallisation from a water/methanol mixture. They were obtained as the methanol solvate [Co(oda)(dpp)(H$_2$O)]·H$_2$O·1/2MeOH and analysed by X-ray crystallography.

[{Co(oda)(H$_2$O)$_2$}$_2$(μ-4,4′-bipy)]·2H$_2$O (9): A solution of 4,4′-bipy (0.078 g, 0.5 mmol) in 25 mL of water was added to a solution of [{Co(oda)(H$_2$O)$_2$}·H$_2$O]$_n$ (0.244 g, 1 mmol) in 25 mL of water. The resulting pink solution was stirred for a few minutes. Complex **9** crystallised upon slow evaporation of the solvent at room temperature. The solid was filtered off, washed with cold water, acetone and diethyl ether and dried in air (0.27 g, 84% yield). Recrystallisation of the product from water resulted in the formation of crystals suitable for an X-ray study. IR: $\tilde{v}$ = 3520–3034 (br), 1642 (s), 1600 (vs), 1534 (w), 1492 (m), 1442 (m), 1407 (s), 1346 (w), 1303 (m), 1226 (w), 1132 (s), 1075 (m), 1028 (m), 922 (m), 814 (m), 725 (w), 638 (m) cm^{-1}. μ_{eff} = 4.4 μ_B at 23 °C. $C_9H_{14}CoNO_8$ (323.14): calcd. C 33.43, H 4.33, N 4.33; found C 33.58, H 4.31, N 4.51.

X-ray Crystallographic Studies: A summary of the crystal data of complexes **2** and **6–9** is given in Table 6. The X-ray data were collected with three different equipments: an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo-K_α radiation (for **2**, **8** and **9**), a Phillips PW1100 FEBO diffractometer equipped with a graphite monochromator and Cu-K_α radiation (for **6**) and a Bruker–Nonius X8APEX-II CCD diffractometer equipped with a graphite monochromator and Mo-K_α radiation (for **7**). The intensities collected for complexes **2**, **6**, **8** and **9** were corrected for Lorenz and polarisation effects. Three standard reflections were monitored every 2 h during the data collection. The atomic scattering factors are those reported by Cromer and Waber.[28] The structures were solved by direct methods using the SIR97 program.[29] The refinements were made by full-matrix least-squares on all F^2 data using SHELXL97.[30] Anisotropic thermal parameters were allotted to all non-hydrogen atoms. The hydrogen atoms of the water bonded to the metal as well as in the free water, when found in the Fourier maps, were refined with an isotropic structure factor, while the other hydrogen atoms were introduced in their calculated positions. The data set for complex **7** was reduced[31] and corrected for Lorentz polarisation effects and absorption by multiscan method applied by SADABS.[32] The structure was solved by direct methods (SIR-2002)[33] and refined

Table 6. Crystal data and structure refinement for complexes **2** and **6**–**9**.

	2	**6**	**7**	**8**	**9**
Formula	$C_{14}H_{22}CoN_2O_9S$	$C_{26}H_{29}CoN_4O_{11}S$	$C_{44}H_{66}Co_2N_4O_{15}$	$C_{37}H_{40}Co_2N_8O_{15}$	$C_{18}H_{28}Co_2N_2O_{16}$
M	453.33	664.53	1008.87	954.63	646.28
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P2_1/n$	$C2/m$
a [Å]	9.1205(14)	8.646(5)	13.547(2)	7.231(3)	10.138(3)
b [Å]	10.793(3)	11.991(5)	10.5035(17)	10.367(2)	20.4555(19)
c [Å]	11.5570(12)	14.537(5)	17.916(3)	26.772(9)	6.130(8)
α [°]	101.777(15)	99.960(5)	90	90	90
β [°]	103.166(12)	104.174(5)	105.889(6)	94.28(3)	103.829(19)
γ [°]	113.85(2)	93.015(5)	90	90	90
V [Å]^3	955.4(3)	1432.1(11)	2451.8(7)	2001.3(11)	1234.3(17)
Z	2	2	2	2	2
$D_{calcd.}$ [Mg m^{-3}]	1.576	1.541	1.367	1.584	1.739
μ [mm^{-1}]	1.057	5.972	0.745	0.911	1.426
T [K]	293(2)	293(2)	173(2)	293(2)	293(2)
$F(000)$	470	688	1064	984	664
Independent reflections	3352	3600	14711	3511	1127
R [$I > 2\theta(I)$]	0.0273	0.0624	0.0452	0.0428	0.0320
wR_2 (all data)	0.0762	0.1605	0.1340	0.1296	0.0890

against all F^2 data by full-matrix least-squares techniques.[34] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined as riding on their respective carbon atoms with isotropic displacement parameters.

CCDC-263308, -263309, -629951, -629952, and -629953 (for **2** and **6**–**9**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): IR spectra of complexes **1a** and **1b**, hydrogen-bonding network of **2** and several plots of structural analyses for cobalt oda and tda compounds.

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