Crystal Structures of Oxalato and Oxamido Polyaminecobalt(III) Complexes Produced by Hydrolysis of Monooxamide

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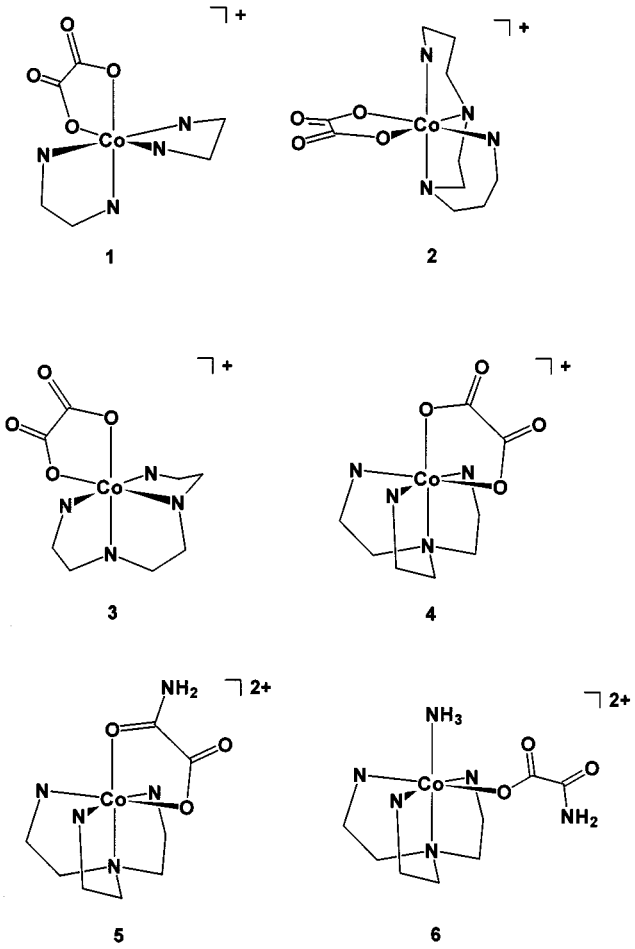
The reactions of sodium monooxamide (H_2NCOCO_2Na) with *trans*-[Co(en)$_2$Cl$_2$]Cl, *trans*-[Co(3,2,3-tet)Cl$_2$]Cl (3,2,3-tet = 1,5,8,12-tetraazadodecane), *cis*-α-[Co(trien)Cl$_2$]Cl and [Co(tren)Cl$_2$]Cl result in the formation of [Co(en)$_2$(ox)]Cl · 4H_2O (**1**), *cis*-β-[Co(3,2,3-tet)(ox)]Cl· 4 H_2O (**2**), *cis*-α-[Co(trien)(ox)]Cl · 2 H_2O (**3**), and [Co(tren)(ox)](ClO_4) · 0.5 H_2O (**4**) respectively, implying a hydrolytic cleavage of the amide bond. [Co(tren)(*O*,*O*′-oxam)]Cl$_2$ · 2 H_2O (**5**) (oxam = $H_2NCOCO_2^-$) and *p*-[Co(tren)(NH_3)(*O*-oxam)]Cl$_2$ (**6**) have also been prepared in order to give mechanistic information for the hydrolysis of monooxamide. Crystal structures of the products are reported and possible pathways for the hydrolysis reactions are discussed.

Since we discovered[1] that compounds of composition [Co(en)$_2$(ox)]X · **n** H_2O (X = Cl^-, *n* = 4; X = Br^-, *n* = 1; X = I^-, *n* = 0) crystallize as conglomerates (conglomerate crystallization is a spontaneous resolution of a racemic solution by crystallization), we have decided to explore the effect of substituting the oxalato ligand with monooxamide ($H_2NCOCO_2^-$) in order to know whether it will displace *cis*- or *trans*-dichloro ligands of Co^{III} to act as a bidentate ligand as oxalate does, and whether additional hydrogen atoms of the NH_2 group will play a major role in their crystallization modes. Much to our surprise, the original purpose in designing this study has not been accomplished since the reaction products we isolated are not monooxamides; instead, they are oxalates obtained by the hydrolysis of the amide bond of the monooxamide anion.

Realizing that this hydrolysis occurs by dichlorocobalt(III) complexes with various types of multidentate polyamine ligands, such as (en)$_2$, 3,2,3-tet, or trien, we thought that we could obtain more detailed information about the hydrolysis of monooxamide including the reaction pathway if a Co^{III} compound with monodentate or bidentate monooxamide could be isolated and characterized unequivocally. *p*-[Co(tren)(NH_3)Cl]$^{2+}$ (the prefix *p*- denotes that the chloro ligand is *trans* to the primary nitrogen atom of the tren ligand) and [Co(tren)Cl$_2$]$^+$ ions were used for that purpose and *O*-bound monodentate and *O*,*O*′-bound bidentate monooxamidecobalt(III) complexes were obtained, respectively.

Although several studies describing the "catalytic" effects of Co^{III} complexes such as *cis*-[$CoN_4(OH_2)(OH)$]$^{2+}$, where N_4 is trien,[2] two ethylenediamines,[3] and tren,[4] and [Co(dien)X][5] (X = tripeptides) on the hydrolysis of amides and peptides have been reported, an amide hydrolysis has not previously been observed with *cis*- or *trans*-dihalo compounds of Co^{III} as in the case of **1**−**4**. Also the formation of oxamido compounds **5** and **6** is unique in that no trivalent transition metal compound containing monooxamide as a monodentate or bidentate ligand has been structurally characterized.



Scheme 1. Line-drawing formulas of the cations of compounds **1**−**6**

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Results and Discussion

In an attempt to probe the effect of exchanging monooxamide for oxalate ligands and recording its crystallization behavior we found that we had not prepared the desired $[Co(en)_2(O,O'\text{-oxam})]Cl_2$. Instead, we isolated the known conglomerate of oxalato compound **1** which suggests that the monooxamide anion had undergone hydrolysis at the amide bond. These results are reproducible and it makes no difference whether one uses the *cis* or *trans* isomer of the dichloro derivative. The structure of the resulting oxalato compound is identical with the published one[1] (see crystallography section).

In order to test the generality of the above observation, we treated the *trans*-$[Co(3,2,3\text{-tet})Cl_2]^+$ ion with sodium monooxamide, which resulted in the formation of the new compound **2**. Its structure (Figure 1) shows that the Co(3,2,3-tet) moiety displays the *cis*-β configuration and that the oxalato ligand faces an asymmetric surface in which one carbonyl group faces two chelate rings (a five- and a six-membered ring) and the other carbonyl group faces a single, six-membered ring, leading to two separate peaks for the carbonyl carbon atoms in the ^{13}C-NMR spectrum (see Experimental Section).

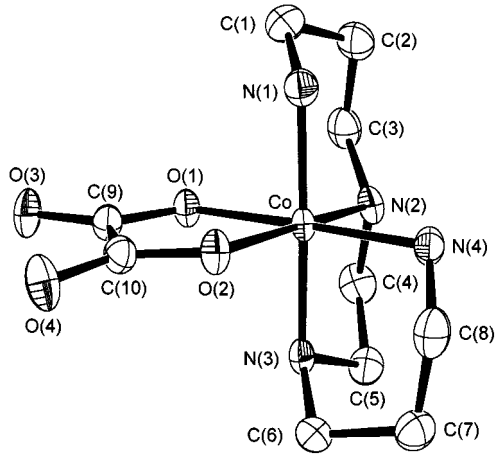


Figure 1. Structure of the cation of **2** drawn at 50% probability level; hydrogen atoms have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.968(2), Co−N(2) 1.959(2), Co−N(3) 1.961(2), Co−N(4) 1.963(2), Co−O(1) 1.912(2), Co−O(2) 1.921(2) Å; O(1)−Co−O(2) 85.21(7), O(1)−Co−N(2) 89.00(8), O(2)−Co−N(4) 91.86(8), O(1)−Co−N(4) 176.99(8), O(2)−Co−N(2) 173.44(8), N(1)−Co−N(3) 178.66(10)°

Compound **3** whose structure is shown in Figure 2 is the product of the reaction of the *cis*-α-$[Co(trien)Cl_2]^+$ ion with sodium monooxamide and indicates the generality of the reaction of *cis*- and *trans*-dichloropolyaminecobalt(III) with monooxamide.

Interestingly, a compound of composition $\{cis\text{-}\alpha\text{-}[Co(trien)(ox)]Cl\}_2 \cdot 9\ H_2O$ was prepared by rational methods and its structure has been reported by this group.[6] The only difference between the two is the number of waters of hydration, a phenomenon which seems to be common in coordination compounds as observed earlier and discussed in some detail.[7] It also would be interesting to note that

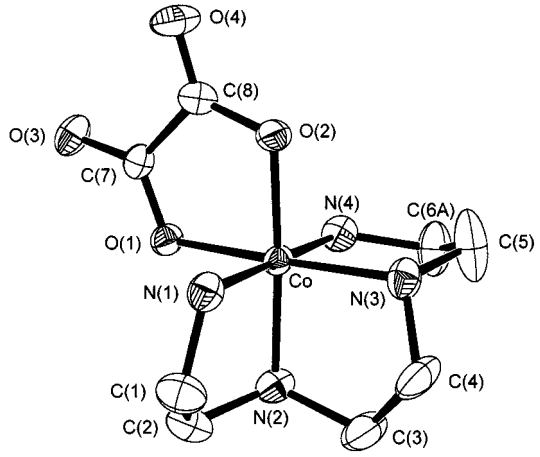


Figure 2. Structure of the cation of **3** drawn without hydrogen atoms; note that C(6) is disordered over two positions corresponding δ and λ conformations and only the former is shown; selected bond lengths and angles: Co−N(1) 1.958(3), Co−N(2) 1.940(3), Co−N(3) 1.943(3), Co−N(4) 1.949(3), Co−O(1) 1.908(2), Co−O(2) 1.906(2) Å; O(1)−Co−O(2) 85.60(10), O(1)−Co−N(2) 93.50(11), O(2)−Co−N(3) 93.80(11), O(1)−Co−N(3) 175.33(11), O(2)−Co−N(2) 174.93(11), N(1)−Co−N(4) 178.65(12)°

the crystal structure of the same compound as **3** but with *cis*-β configuration has been reported.[8]

Compound **4** whose crystal structure has not been reported was prepared by simple ligand displacement of chlorides with oxalate or by base hydrolysis of monooxamide with $[Co(tren)Cl_2]Cl$. As the structure of the cation shown in Figure 3 implies, only one peak is observed for the carbonyl carbon atoms in the ^{13}C-NMR spectrum. The crystallographic asymmetric unit of compound **4** contains two independent molecules and the two molecules are different only in that the five-membered chelate ring which is *trans* to the oxalato ligand has δ and λ conformations in Co(1a) and Co(1b) cations, respectively.

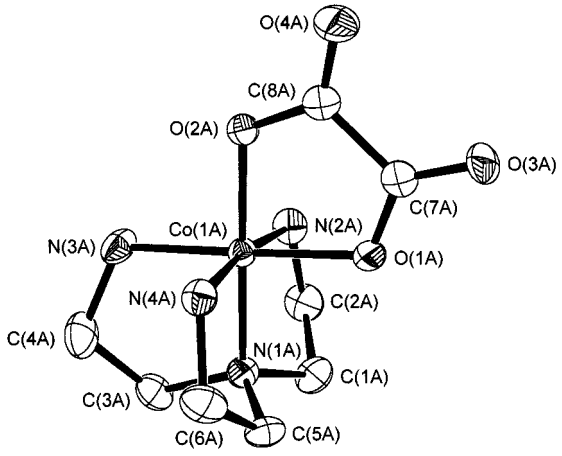


Figure 3. Structure of one of the two cations of **4**; the three chelate rings of tren ligand have (λδδ) conformation; the Co(1b) cation which is not shown here has (λλδ) conformation; selected bond lengths and angles: Co(1a)−N(1a) 1.936(4), Co(1a)−N(2a) 1.954(4), Co(1a)−N(3a) 1.938(4), Co(1a)−N(4a) 1.951(4), Co(1a)−O(1a) 1.925(3), Co(1a)−O(2a) 1.906(3) Å; O(1a)−Co(1a)−O(2a) 85.18(14), O(1a)−Co(1a)−N(1a) 94.2(2), O(2a)−Co(1a)−N(3a) 93.2(2), O(1a)−Co(1a)−N(3a) 177.9(2), O(2a)−Co(1a)−N(1a) 179.4(2), N(2a)−Co(1a)−N(4a) 171.9(2)°

When $[Co(tren)Cl_2]Cl$ was allowed to react with monooxamide in a neutral aqueous solution in a temperature range of 20−45°C, the hydrolysis does not occur and both chloro ligands are replaced by *O*,*O*′-bound monooxamide to give compound **5**. The structure of the cation is shown in Figure 4 and two separate peaks for the carbonyl carbon atoms are observed in the ^{13}C-NMR spectrum, as expected.

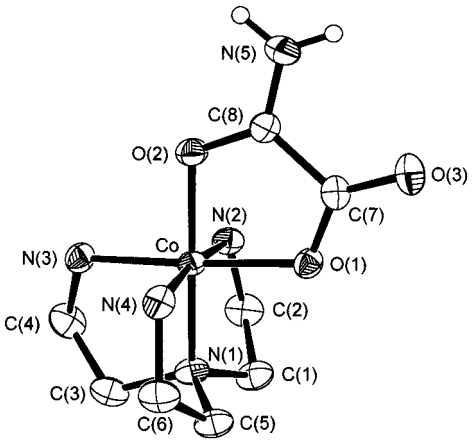


Figure 4. Structure of the cation of **5** showing the bidentate monooxamide ligand; hydrogen atoms of the tren ligand have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.918(3), Co−N(2) 1.957(3), Co−N(3) 1.931(3), Co−N(4) 1.957(3), Co−O(1) 1.929(2), Co−O(2) 1.917(3) C(8)−N(5) 1.299(5) Å; O(1)−Co−O(2) 85.00(11), O(1)−Co−N(1) 94.80(13), O(2)−Co−N(3) 92.51(13), O(1)−Co−N(3) 177.01(13), O(2)−Co−N(1) 179.63(12), N(2)−Co−N(4) 172.53(13)°

The Cambridge Structural Database[9] lists three transition metal compounds which contain bidentate *O*,*O*′-bound monooxamide ligands. They are of the structure type $[M(O,O'\text{-oxam})_2(H_2O)_x] \cdot n\ H_2O$ (M = Co^{2+}, $x = 2$, $n = 2$[10]; M = Zn^{2+}, $x = 2$, $n = 0$[11]; M = Cd^{2+}, $x = 4$, $n = 0$[12]). Note that all of them bore divalent metal cations.

Finally, the *p*-$[Co(tren)(NH_3)Cl]^{2+}$ ion was treated with monooxamide to give compound **6**. The structure of the cation (Figure 5) shows that only the chloro ligand has been replaced, as expected, by a monodentate *O*-bound monooxamide whose amide bond is still intact, which suggests that an unactivated amide bond of monooxamide would not easily be hydrolyzed, if at all.

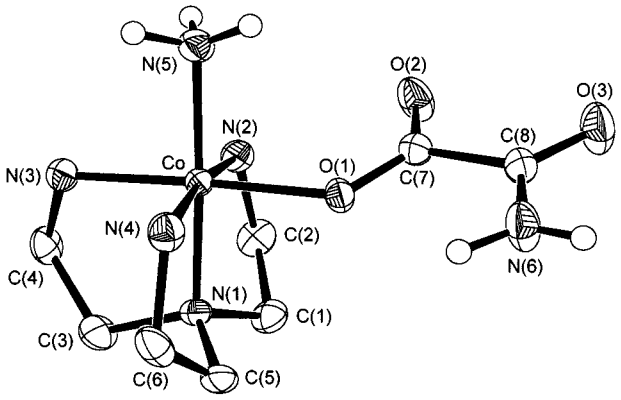
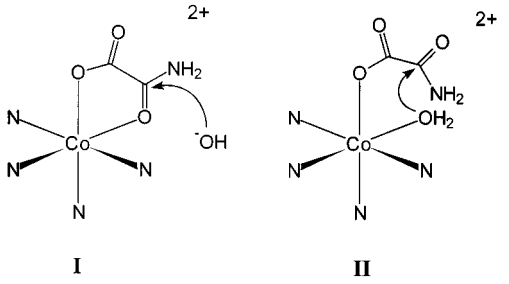


Figure 5. Structure of the cation of **6** showing the dangling NH_2 group of the monodentate monooxamide ligand; hydrogen atoms of the tren ligand have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.949(2), Co−N(2) 1.970(2), Co−N(3) 1.927(3), Co−N(4) 1.960(3), Co−O(1) 1.949(2), Co−N(5) 1.943(2) C(8)−N(6) 1.321(4) Å; O(1)−Co−N(2) 92.47(10), O(1)−Co−N(4) 83.24(10), O(1)−Co−N(5) 91.13(10), O(1)−Co−N(3) 175.53(10), N(5)−Co−N(1) 177.36(11), N(2)−Co−N(4) 171.19(11)°

As far as we know, a transition metal compound containing a monodentate monooxamide ligand has never been structurally characterized.

As reviewed earlier,[13] two reaction pathways, the so-called "direct activation" and "intramolecular attack", have been postulated for the hydrolysis of amide bonds by Co^{III} complexes. Although a detailed discussion concerning the hydrolysis mechanism can not be made without kinetic data obtained under pH-controlled condition, two key intermediates can be considered for this work according to the above concepts (Scheme 2).



Scheme 2. Key step for direct activation (**I**) and intramolecular attack (**II**)

Species **I** and **II** correspond to the direct activation and intramolecular attack, respectively. For compounds **1**−**3**, the possibility of hydrolysis through intermediate **I** can be excluded for the following reasons. First, relatively flexible binding modes of $(en)_2$, 3,2,3-tet, or trien coupled with labile chloro ligands would allow coordination of a solvent water molecule before monooxamide became a bidentate ligand. This is especially true for **1** and **2** which undergo *trans*/*cis* isomerization at raised temperature. Second, "neutral", deionized, solvent water used in this work was in fact slightly acidic (pH = 5.40) due to atmospheric CO_2, which makes the attack of HO^- ion to the amide carbon atom less likely to occur. The possibility of attack of solvent water to bidentate monooxamide can also be removed as the presence of compound **5** implies. Therefore, we cautiously adopt the intramolecular attack of a coordinated water molecule as the correct mechanism for the hydrolysis of monooxamide by Co^{III} complexes with configurationally versatile multidentate amine ligands.

The behavior of monooxamide with $[Co(tren)Cl_2]Cl$ also supports this argument. That is, when the multidentate amine ligand of a Co^{III} complex is configurationally rigid and chloro ligands are relatively stable with respect to the substitution by solvent water molecules, monooxamide coordinates as a bidentate ligand as in compound **5** and the hydrolysis of the amide bond does not occur. Once monooxamide is coordinated as a bidentate ligand, an additional source of HO^- ions is necessary in order to hydrolyze the amide bond.

In conclusion, monooxamide was found to be hydrolyzed by Co^{III} complexes containing various types of polyamine tetradentate ligands, such as $(en)_2$, 3,2,3-tet, trien, or tren to give their corresponding oxalato compounds **1**, **2**, **3**, and **4**, respectively. In compounds **1**, **2**, and **3**, intramolecular attack of coordinated water molecule is the likely pathway for the hydrolysis reactions. In compound **4**, the hydrolysis reaction seems to occur by attack of HO^- ions to the amide carbon atom of the bidentate monooxamide ligand. Compounds **5** and **6** are also important not only from their structural point of view, but also because of their implications in the hydrolysis mechanism.

Experimental Section

General: H_2NCOCO_2Na (Aldrich Chemical Company) and $(NH_4)_2C_2O_4 \cdot H_2O$ (Fisher Scientific Company) were used as received. *trans*-$[Co(en)_2Cl_2]Cl$,[14] *trans*-$[Co(3,2,3\text{-tet})Cl_2]Cl$,[15] *cis*-α-$[Co(trien)Cl_2]Cl \cdot 2\ H_2O$,[7] $[Co(tren)Cl_2]Cl$,[16] and *p*-$[Co(tren)(NH_3)Cl]Cl(ClO_4)$[17] were prepared using known methods. Elemental analyses were carried out by the Galbraith laboratories.[18] ^{13}C-NMR spectra were recorded with a GE QE-300 instrument using TMSPA as the internal standard.

$[Co(en)_2(ox)]Cl \cdot 4\ H_2O$ (1): 30 mL of an aqueous solution of 2.00 g (18 mmol) of H_2NCOCO_2Na was slowly added to a greenish solution of 4.08 g (14 mmol) of *trans*-$[Co(en)_2Cl_2]Cl$ in 30 mL of water. While heating the solution at 60°C, the color changed to purple and finally to red. When the volume was reduced to about 15 mL, it was allowed to stand at room temperature. After 10 d, red crystals were obtained which effloresce upon removal from the mother liquor. The compound was analyzed after drying to constant weight. − $C_6H_{16}ClCoN_4O_4$ (302.64): calcd. C 23.81, H 5.34, N 18.52; found C 22.55, H 5.59, N 17.90.

***cis*-β-[Co(3,2,3-tet)(ox)]Cl · 4 H_2O (2):** The same procedure as in the case of **1** was employed using *trans*-$[Co(3,2,3\text{-tet})Cl_2]Cl$. Red crystals were obtained after 10 d at room temperature. − $C_{10}H_{30}ClCoN_4O_8$ (428.76): calcd. C 28.01, H 7.07, N 13.07; found C 27.95, H 6.98, N 13.20. − ^{13}C NMR (300 MHz, D_2O): δ = 168.38 and 168.44 (2 C=O), 20.97, 26.01, 37.69, 38.22, 44.74, 47,49, 48.45, and 53.37 (8 CH_2).

***cis*-α-[Co(trien)(ox)]Cl · 2 H_2O (3):** The same procedure as in the case of **1** was used by treating equimolar amounts of *cis*-α-$[Co(trien)Cl_2]Cl \cdot 2\ H_2O$ and H_2NCOCO_2Na. Red crystals were collected after 3 weeks. − $C_8H_{22}ClCoN_4O_6$ (364.67): calcd. C 26.35, H 6.08, N 15.36; found C 25.80, H 6.08, N 15.46.

$[Co(tren)(ox)]ClO_4 \cdot 0.5\ H_2O$ (4): ***Warning: Metal amine perchlorates may be explosive!*** A solution of ammonium oxalate (0.46 g, 3.24 mmol) in 11 mL of water was added to a solution of $[Co(tren)Cl_2]Cl$ (1.00 g, 3.21 mmol) in 12 mL of water. The initially formed purple precipitate dissolved and the solution turned a clear red color after heating for 10 min; 0.40 g (3.27 mmol) of $NaClO_4$ was then added and the solution was filtered. Red crystals were formed upon standing and collected after 2 weeks (0.99 g, 77%). − $C_8H_{19}ClCoN_4O_{8.5}$ (401.65): calcd. C 23.92, H 4.77, N 13.95; found C 23.70, H 4.87, N 13.90. − ^{13}C NMR (300 MHz, D_2O):

Table 1. Summary of crystal data and structure refinement for oxalato compounds **2**, **3**, and **4**

	2	**3**	**4**
Empirical formula	$C_{10}H_{30}ClCoN_4O_8$	$C_8H_{22}ClCoN_4O_6$	$C_8H_{19}ClCoN_4O_{8.5}$
Molecular mass	428.76	364.68	401.65
T [K]		293(2)	
λ [Å]		0.71073	
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.186(2)	6.996(4)	11.1307(13)
b [Å]	15.508(7)	8.822(1)	11.508(2)
c [Å]	14.569(3)	12.537(2)	11.595(4)
α [°]	90	89.13(2)	97.45(2)
β [°]	102.53(1)	75.72(3)	90.609(12)
γ [°]	90	81.39(3)	97.955(12)
V [Å^3]	1805.6(9)	741.2(5)	1457.9(6)
Z	4	2	4
$D_{calcd.}$ [g/cm^3]	1.577	1.634	1.830
μ [mm^{-1}]	1.143	1.367	1.412
F(000)	904	380	828
Crystal size [mm]	0.53 × 0.34 × 0.29	0.49 × 0.17 × 0.16	0.50 × 0.30 × 0.26
θ range [°]	2 to 25	2 to 25	2 to 25
Index ranges (h, k, l)	±9, +18, +17	±8, ±10, +14	+13, ±13, ±13
Reflections collected	3387	2729	5392
independent (R_{int})	3163 (0.0212)	2597 (0.0247)	5107 (0.0634)
observed [I>2σ(I)]	2270	1844	3159
Absorption correction		ψ scan	
Transmission	0.9996−0.8779	0.9965−0.9382	0.9930−0.8425
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/param.	3163/0/337	2597/0/208	5107/2/414
GOF on F^2	0.972	1.094	1.042
R indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0266	R_1 = 0.0334	R_1 = 0.0480
	wR_2 = 0.0617	wR_2 = 0.0877	wR_2 = 0.1291
R indices (all data)	R_1 = 0.0543	R_1 = 0.0653	R_1 = 0.0995
	wR_2 = 0.0667	wR_2 = 0.0950	wR_2 = 0.1415
Largest diff. peak and hole [e/Å^3]	0.228 and −0.276	0.436 and −0.290	1.373 and −0.648

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ and $w = 1/[\sigma^2F_o^2 + (a \cdot P)^2]$, where $P = (F_o^2 + 2\ F_c^2)/3$.

δ = 166.57 (2 C=O), 43.38, 44.12, 59.47, and 61.56 (6 CH_2). − The same product was obtained by adding 0.21 g (5.25 mmol) of NaOH to a solution containing 1.00 g (3.21 mmol) of [Co(tren)Cl_2]Cl and 0.36 g (3.24 mmol) of H_2NCOCO_2Na in 15 mL of water. The resulting dark red solution was filtered after stirring for 30 min; 0.4 g (3.27 mmol) of $NaClO_4$ was added to the solution after 5 d and the solution was filtered. The solution was filtered off frequently whenever a powdery precipitate was formed until red single-crystals suitable for X-ray diffraction study were obtained. The unit cell parameters [a = 11.1569(21), b = 11.5038(22), c = 11.5904(117) Å, α = 97.377(35), β = 90.782(31), γ = 97.974(14)°] and the Laue class of the unit cell were identical, within experimental error, with those of the compound prepared from ammonium oxalate, and therefore X-ray data were not collected. − calcd. C 23.92, H 4.77, N 13.95; found C 23.64, H 5.03, N 13.91.

[Co(tren)(O,O′-oxam)]Cl_2 · 2 H_2O (5): A mixture of 0.18 g (1.62 mmol) of H_2NCOCO_2Na in 3 mL and 0.50 g (1.61 mmol) of [Co(tren)Cl_2]Cl in 10 mL of water was stirred for 30 min at room temperature and then filtered. Red plate crystals were obtained upon standing and collected after 8 d (0.58 g, 90%). − $C_8H_{24}Cl_2CoN_5O_5$ (400.15): calcd. C 24.01, H 6.05, N 17.50; found C 22.75, H 5.68, N 16.21. Although duplicate analyses were carried out due to the disagreement between calculated and experimental results, all the experimental values were consistently smaller than calculated values. Because there is no doubt in the crystal structure and because the ratio of the number of each element to the other showed good agreement with calculated values, the apparent disagreement was ignored. − ^{13}C NMR (300 MHz, D_2O): δ = 166.53 [C(=O)O], 170.67 [C(=O)NH_2], 43.72, 44.13, 60.68, and 62.91 (6 CH_2). − In a separate experiment, the initial reaction mixture was warmed at 45°C for 30 min and then filtered. The purple solution turned red within 4 h. Red plate crystals were obtained upon standing and examined on a X-ray diffractometer to give the same unit cell parameters [a = 11.2172(45), b = 22.4952(76), c = 12.8525(120) Å, α = β = γ = 90°] and Laue symmetry as the compound obtained from the room-temperature reaction, and therefore X-ray data were not collected. − ^{13}C NMR (300 MHz, D_2O): δ = 166.50 [C(=O)O], 170.69 [C(=O)NH_2], 43.55, 43.96, 60.47, and 62.73 (6 CH_2).

***p*-[Co(tren)(NH_3)(O-oxam)]Cl_2 (6):** A partly dissolved solution containing 1.12 g (2.85 mmol) of *p*-[Co(tren)(NH_3)Cl]Cl(ClO_4) in 20 mL of water was directly filtered into a solution of H_2NCOCO_2Na (0.32 g, 2.88 mmol) in 10 mL of water. Small amounts of red crystals suitable for X-ray diffraction were obtained by liquid diffusion with acetone and collected after 10 d. − $C_8H_{23}Cl_2CoN_6O_3$ (381.15): calcd. C 25.21, H 6.09, N 22.05; found C 25.18, H 6.19, N 21.95.

Crystallography: For all six compounds the intensity data were collected with an Enraf-Nonius CAD4 diffractometer. Although the crystal of **1** was mounted inside a sealed capillary tube in order to prevent decay, it completely lost its crystallinity after collecting 1267 reflections with a total X-ray exposure time of 82387 s (22.87 h). The unit cell was orthorhombic with a = 6.340(3), b = 11.976(3), and c = 20.290(6). The limited data set showed only three systematic absences, $h \neq 2n$ for (h00), $k \neq 2n$ for (0k0) and $l \neq 2n$ for (00l), implying the unique space group $P2_12_12_1$ (no. 19). It was then noticed that the symmetry and unit cell dimensions agree with [Co(en)$_2$(ox)]Cl · 4 H_2O of ref.[1], which is orthorhombic, $P2_12_12_1$, a = 6.349(3), b = 11.969(4), and c = 20.311(5), and isotropic refinement of the structure using the atomic coordinates from the reference gave an R factor of 16% for 413 observed reflections [$I > 2\sigma(I)$]. For the compounds **2**−**6** routine procedures were used to collect data and solve the structures. Hydrogen atoms of **3**, **4**, and **5** were placed in their geometrically ideal positions with isotropic temperature factors 1.2 times of those of the attached non-hydrogen atoms. However, hydrogen atoms of water molecules and monooxamide ligand of those compounds along with all hydrogen atoms of **2** and **6** were located from difference maps and refined isotropically. SHELXS-86[19] and SHELXL-93[20] were used for solution and refinement, respectively. Parameters for data collection and structure refinements are summarized in Table 1 and 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre[9] as supplementary publication no. CCDC-111984 to CCDC-111988.

Table 2. Summary of crystal data and structure refinement for oxamido compounds **5** and **6**

	5	**6**
rEmpirical formula	$C_8H_{24}Cl_2CoN_5O_5$	$C_8H_{23}Cl_2CoN_6O_3$
Molecular mass	400.15	381.15
T [K]	293(2)	
λ [Å]	0.71073	
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a [Å]	11.2213(9)	8.212(2)
b [Å]	22.502(2)	10.941(2)
c [Å]	12.913(2)	16.881(3)
β [°]	90	92.45(1)
V [Å^3]	3260.7(6)	1515.4(5)
Z	8	4
$D_{calcd.}$ [g/cm^3]	1.630	1.671
μ [mm^{-1}]	1.407	1.501
F(000)	1664	792
Crystal size [mm]	0.69 × 0.67 × 0.34	0.60 × 0.33 × 0.27
θ range [°]	2 to 25	2 to 25
Index ranges (h, k, l)	+13, +26, +15	±9, +12, +20
Reflections collected	2857	2745
iIndependent (R_{int})	2857 (0.0000)	2657 (0.0190)
observed [$I>2\sigma(I)$]	1678	1881
Absorption correction	ψ scan	
Transmission	0.9995−0.6583	0.9940−0.8514
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/ parameters	2857/0/215	2657/0/273
GOF on F^2	0.958	1.014
R indices [$I > 2\sigma(I)$]	R_1 = 0.0347, wR_2 = 0.0876	R_1 = 0.0287, wR_2 = 0.0724
R indices (all data)	R_1 = 0.0913, wR_2 = 0.0996	R_1 = 0.0543, wR_2 = 0.0781
Extinction coefficient	0.0071(4)	−
Largest diff. peak and hole [e/Å^3]	0.429 and −0.436	0.421 and −0.371

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