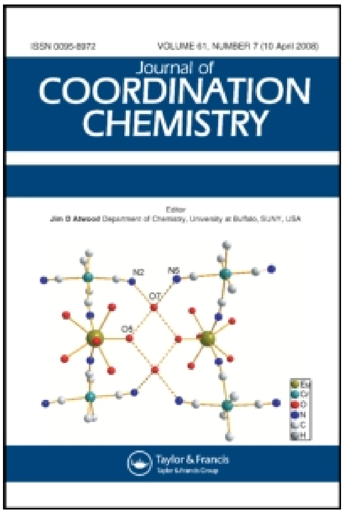

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

LIGAND DISPLACEMENT REACTIONS FROM THE COORDINATION SPHERE OF [*CIS*-CO$(NH_3)_4(NO_2)_2$]NO_3: THE CRYSTAL AND MOLECULAR STRUCTURES OF [*CIS*-CO$(NH_3)_4$(OH)CL]CL (I) AND [CO$(NH_3)_4$(OXALATO)]$_2$[*TRANS*-(NH_3)(OH)CO(OXALATO)$_2$]·$4H_2O$ (II)

Ivan Bernal[a]; James Cetrullo[a]; Jozef Myrczek[ab]
[a] Chemistry Department, University of Houston, Houston, TX, U.S.A. [b] Technical University of Wroclaw, Wroclaw, Poland

To cite this Article Bernal, Ivan , Cetrullo, James and Myrczek, Jozef(1993) 'LIGAND DISPLACEMENT REACTIONS FROM THE COORDINATION SPHERE OF [*CIS*-CO$(NH_3)_4(NO_2)_2$]NO_3: THE CRYSTAL AND MOLECULAR STRUCTURES OF [*CIS*-CO$(NH_3)_4$(OH)CL]CL (I) AND [CO$(NH_3)_4$(OXALATO)]$_2$[*TRANS*-(NH_3)(OH)CO(OXALATO)$_2$]·$4H_2O$ (II)', Journal of Coordination Chemistry, 30: 3, 367 — 378
To link to this Article: DOI: 10.1080/00958979308022770
URL: http://dx.doi.org/10.1080/00958979308022770

J. Coord. Chem., 1993, Vol 30, pp. 367–378
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LIGAND DISPLACEMENT REACTIONS FROM THE COORDINATION SPHERE OF $[\textit{CIS}\text{-}CO(NH_3)_4(NO_2)_2]NO_3$: THE CRYSTAL AND MOLECULAR STRUCTURES OF $[\textit{CIS}\text{-}CO(NH_3)_4(OH)CL]CL$ (I) AND $[CO(NH_3)_4(OXALATO)]_2[\textit{TRANS}\text{-}(NH_3)(OH)CO(OXALATO)_2]\cdot 4H_2O$ (II)

IVAN BERNAL*, JAMES CETRULLO† and JOZEF MYRCZEK†#

Chemistry Department, University of Houston, Houston, TX 77204-5641, U.S.A.

(Received September 21, 1992)

Compound (I) crystallizes in the space group *Pnma* with cell constants $a = 13.295(2)$, $b = 10.320(1)$, $c = 6.732(1)$; $V = 923.63$ Å^3, d(calc; $M = 214.97$, $z = 4$) = 1.546 gm cm^{-3}. Data (2340 total reflections) were collected over the range $4° \leq 2\Theta \leq 70°$ and corrected for absorption ($\mu = 23.804$ cm^{-1}). The cation is a *cis*-chlorohydroxo species in which all the hydrogen atoms were accurately located and refined. Refinement of the heavy atoms with anisotropic thermal parameters and of the hydrogen atom positions ($B = 4.0$ Å^2, fixed) led to the final $R(F)$ and $R_w(F)$ factors of 0.033 and 0.039, respectively.

Compound (II) crystallizes in the monoclinic space group $P2_1/n$ with cell constants $a = 11.429(2)$, $b = 8.298(2)$, $c = 14.512(2)$Å, $\beta = 102.25°$; $V = 1344.895$ Å^3; d(meas., picnometer) = 1.845 gm cm^{-3}, d(calc; $M = 771.22$, $Z = 2$) = 1.815 gm cm^{-3}. A total of 3488 unique data were collected over the range $4° \leq 2\Theta \leq 60°$, of which 1976 wee used in the final refinement cycle. The data were corrected for absorption ($\mu = 19.111$ cm^{-1}). The anion of this compound lies on an inversion centre; therefore NH_3 and the OH are disordered. All other hydrogen atoms present in the cation and anion, as well as of the waters of hydration, were located in the X-ray study. Refinement of the heavy atoms with anisotropic thermal parameters while adding the hydrogen atoms as fixed contributions ($B = 4.0$Å^2) produced final values of the discrepancy indices of $R(F) = 0.044$ and $R_w(F) = 0.036$.

Both compounds were obtained during efforts to prepare single crystals of $[Co(NH_3)_4(\text{oxalato})]Cl$ starting from $[Co(NH_3)_4(NO_2)_2](NO_3)$, oxalic acid and NaCl, and their identification is of interest from the standpoint of ligand replacement reactions. The presence or absence of the *trans* effect was investigated and we conclude that this effect can be observed or masked depending on the nature of the charge-compensating ions present in the crystals.

KEYWORDS: Cobalt(III), amine, nitrite, oxalate, reactions, x-ray structure

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* Author for correspondence.

† Fellows of the Robert A. Welch Foundation.

\# On leave from the Technical University of Wroclaw, I-5, Wroclaw, Poland.

INTRODUCTION

As a part of our investigations into the crystallization behaviour of metal amine oxalates, we recently reported[1] the crystal structures of the compounds $[Co(NH_3)_4(oxalato)]NO_3 \cdot H_2O$ (a conglomerate) and $[Co(NH_3)_4(oxalato)]I \cdot H_2O$ (a racemate) and, thus, were interested in the structure of the chloride in order to determine its crystallization pathway. It has long been known that NO_2 ligands can be displaced by carboxylic acids, such as oxalic acid. In fact, such a displacement of ligands was used in the past as an argument for assigning geometrical isomerism to certain species. For example, the displacement of NO_2 ligands from Erdmann's salt, $K[Co(NH_3)_2(NO_2)_4]$, was used by Shibata[2] in 1916 to determine whether the anions were *cis* or *trans*. The ensuing controversy this paper created is described in detail by Komiyama.[3]

Finally, we have prepared[4] $NH_4[\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(oxalato)]$ by the ligand displacement method of Ito and Shibata[5] and determined the structure of the anion in the form of the $[\textit{trans}\text{-}Co(en)_2(NO_2)_2][\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(oxalato)]$ and found that, indeed, the amino groups are *trans* to each other. What we found when we attempted to isolate the chloride, by first displacing a pair of NO_2 groups from $[Co(NH_3)_4(NO_2)_2]^+$ with oxalic acid/sodium oxalate, and adding an excess of NaCl to the resulting solution is discussed below.

EXPERIMENTAL

Syntheses

$[\textit{cis}\text{-}Co(NH_3)_4(NO_2)_2]NO_3$ was prepared according to the procedure of Grubitsch.[6] An equimolar amount of this compound and oxalic acid were dissolved, with stirring at 60°C, in a minimum of water and a small excess of NaCl was added, as was done when preparing the iodide.[1] The crystals obtained in this attempt were of $[\textit{cis}\text{-}Co(NH_3)_4(oxalato)]NO_3$; therefore, a large excess of NaCl was added to the same solution and pink crystals were isolated, and which turned out to be compound (I).

Compound (II) was obtained when a mol of both oxalic acid and sodium oxalate and excess NaCl were added, with stirring at 60°C, to the solution of $[\textit{cis}\text{-}Co(NH_3)_4(NO_2)_2]NO_3$. This is probably not the only compound formed during this attempt to synthesize $[Co(NH_3)_4(ox)]Cl$. Instead, we believe, the solution contained a mixture of compounds but the crystallization batch we used for our studies comprised largely (II) since density and elemental analysis agree with the crystallographic formulation and FABS data showed a peak of the correct mass for the ion triplet of (II).

Analyses

Elemental analyses were not carried out on (I) since we had only a very small number of crystals; however, its structure, including hydrogen atoms is so well defined that it constitutes an elemental analysis. FABS data on (II) obtained at the University of Houston shows a peak at 700 mass units, which corresponds to the monoprotonated ion triplet of composition $\{[Co(NH_3]_4(ox)]_2[Co(NH_3)(OH)(ox)_2]H^+\}$, which can be viewed as the FABS protonation of the OH of the bis-oxalato cobalt moiety. Details of FABS acquisition techniques can be found in ref. 7. Elemental analyses[8] give reasonable agreement with the formula for (II). Theory for $Co_3O_{21}N_9C_8H_{36}$: C, 12.46; H, 4.71; N, 16.35; O, 43.57%; found: C, 12.60; H, 4.65; N, 14.87; O, 43.41%. Note, in this context, that the measured density (average of two independent determinations) is a little higher than that calculated from the mass and unit cell volume of (II). This, together with the FABS result, indicate our compositional assignment is reasonable and consistent with the X-Ray results. Density measurements were carried out picnometrically, on (II), in duplicate. Average of two measurements is 1.845 gm cm^{-3}.

X-Ray measurements

Data for both compounds were collected and processed in the same fashion. All data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[9] of the SDP-Plus software package.[10] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for both crystals. They were centred with data in the $18° \leq 2\Theta \leq 30°$ range and examination of the cell constants, absences, and Niggli matrix[11] clearly showed (I) to crystallize in a primitive, orthorhombic lattice whose systematic absences belong to those of the space group *Pnma* or $Pna2_1$. The former was initially assumed and found to be correct from refinement and the distribution of intensities, which was centrosymmetric. Compound (II) crystallizes in the primitive,[11] monoclinic space group $P2_1/n$ since the systematic absences clearly show the presence of a two-fold screw axis and an *n*-glide.

The details of data collection and processing are summarized in Tables 1 and 2, respectively, for compounds (I) and (II). The intensity data sets were corrected for

Table 1 Summary of data collection and processing parameters for [*cis*-$Co(NH_3)_4(OH)Cl$]Cl (I).

Space Group	*Pnma*
Cell Constants	a = 13.295(2)
	b = 10.320(1)
	c = 6.732(2)Å
Cell Volume	V = 923.63 Å^3
Molecular Formula	$CoCl_2ON_4H_{13}$
Molecular Weight	214.97
Density (calc; Z = 4 mol/cell)	1.546 g cm^{-3}
Radiation Employed	MoK_α (λ = 0.71073 Å)
Absorption Coefficient	μ = 23.8 cm^{-1}
Relative Transmission Coefficients	0.7970 to 0.9997
Data Collection Range	$4° \leq 2\Theta \leq 70°$
Scan Width	$\Delta\Theta = 1.0 + 0.35 \tan\Theta$
Total Data Collected	2340
Data Used in Refinement*	1605
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.033
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.039
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 735 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for theabsorption correction, symmetry related, standards or did not meet the criterion that $I \geq 3\sigma(I)$.

Table 2 Summary of data collection and processing parameters for $[Co(NH_3)_4(oxalato)]_2$ [*trans*-$(NH_3)(OH)Co(oxalato)_2] \cdot 4H_2O$ (II).

Space Group	$P2_1/n$
Cell Constants	$a = 11.429(2)$ $b = 8.298(2)$ $c = 14.512(2)$ Å $\beta = 102.25(1)°$
Cell Volume	$V = 1344.895$ Å^3
Molecular Formula	$Co_3O_{21}N_9C_8H_{36}$
Molecular Weight	771.22
Density, measured (picnometry)	1.845 gm cm^{-3}
Density, (calc; $Z = 2$ mol/cell)	1.815 g cm^{-3}
Radiation Employed	MoK_α ($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 19.11$ cm^{-1}
Relative Transmission Coefficients	0.8736 to 0.9997
Data Collection Range	$4° \leq 2\Theta \leq 60°$
Scan Width	$\Delta\Theta = 1.0 + 0.35 \tan\Theta$
Total Data Collected	3488
Data Used In Refinement*	1976
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.044
$R_w = [\Sigma w^2(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.036
Weights Used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 1512 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards or did not meet the criterion that $I \geq 3\sigma(I)$.

absorption using empirical curves derived from Psi scans[9,10] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[12]

The structures were solved from the Patterson maps using Co as the heavy atom. For compound (I), the space group *Pnma* was assumed and found to be correct, since as expected from the cell contents, the Co has to be at a special position (in this case a mirror plane; see below). Eventual refinement results prove the choice of the space group to be justified.

There was no ambiguity about the space group of (II). After refinement of the scale factor and the positional parameters of the two Co atoms, a difference Fourier map produced many of the non-hydrogen atoms. The remaining atoms were found in subsequent difference maps. Heavy atoms were refined isotropically until convergence. Conversion of the heavy atoms to anisotropic motion in the case of (I) resulted in a good quality refinement, as shown by the R factors. For both compounds, we found enough sensibly positioned hydrogen atoms of the amines to be able to calculate the missing ones. As for the hydroxo ligand of (I), its hydrogen was found at an equally sensible position; thus, it added as fixed contributions ($B = 4.00$ Å^2) to the structure factors. In (II), however, the hydroxy ligand is disordered with its *trans*-axial amine; therefore, since two well placed hydrogens were found for the amine (N(1)) the disorder problem was ignored. These procedures resulted in the successful refinement of the structures to final residual values of $R(F) = 0.033$ and $R_w(F) = 0.039$ for (I) and of $R(F) = 0.044$ and of $R_w(F) = 0.036$ for (II).

Figures 1 and 3 give labelled views of the molecules. Figures 2 and 4 depict the packing of the ions in their respective unit cells. Final positional and equivalent isotropic thermal parameters are given in Tables 3 and 4. Bond lengths and angles are listed in Tables 5 and 6.

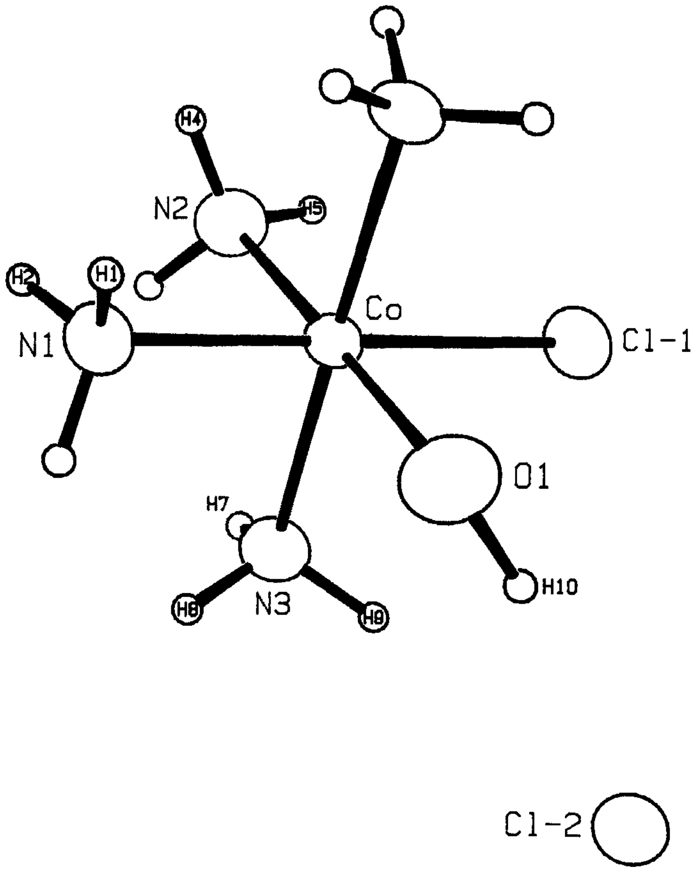

Figure 1 The contents of the asymmetric unit present in compound (I). Note that all hydrogen atoms were found experimentally at the positions shown. The numbering system is described herein.

DISCUSSION

There is no crystallographic disorder or controversial issue regarding the solution and refinement of (I); moreover, judging by the fact that we experimentally found most of the hydrogens of the cation, and that sensible values are obtained for the distances and angles associated with their positions after being refined, the quality of the structural description of the cation present in (I) is more than adequate. For example, the three Co-N distances are 1.954(1), 1.956(1) and 1.959(1) Å. Figure 1 shows that N3 is the amine nitrogen *trans* to another amine (itself, since the mirror converts N3 into the fourth amine of the cation); as such, it should have the longest Co-N distance due to the *trans* effect, and we note that it does. N2 is *trans* to the hydroxo ligand; therefore, it should have the intermediate value of the Co-N bonds, and it does. Finally, the Co-Cl distance is 2.272(1) Å, a result which compares well with the values of 2.270(2), 2.267(2), 2.264(1) and 2.266(1) (av. = 2.268(2) Å) found[13] in two different crystalline polymorphs of [*cis*-α-Co(trien)Cl_2]Cl·nH_2O

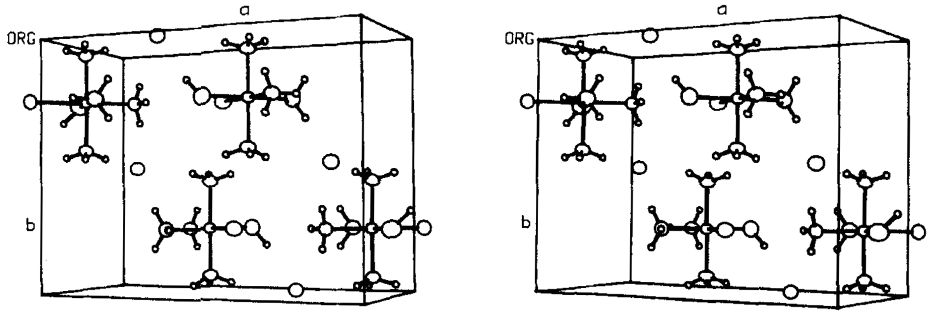

Figure 2 Packing of cations and anions in compound (I). This is a stereo pair.

(n = 2, 3). The Co-O(H) distance is 1.971(1) Å, which is in range of values obtained by Solans, *et al.*,[14] who studied a series of Cr(III) amines containing hydroxide ligands.

The only additional comment we wish to make is that the presence of chlorine in the coordination sphere and as a charge compensating anion is not unexpected in view of the fact that excess NaCl was used. The presence of the hydroxide must

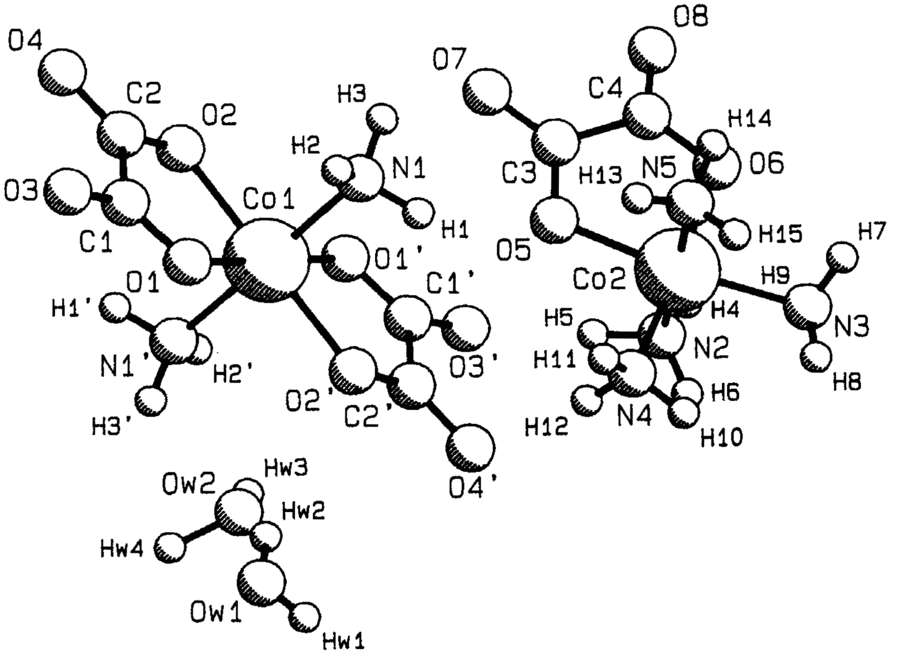

Figure 3 The contents of the asymmetric unit present in compound (II). Note that all hydrogen atoms, including those at the waters of crystallization, were found experimentally at the positions shown. The numbering system is described herein.

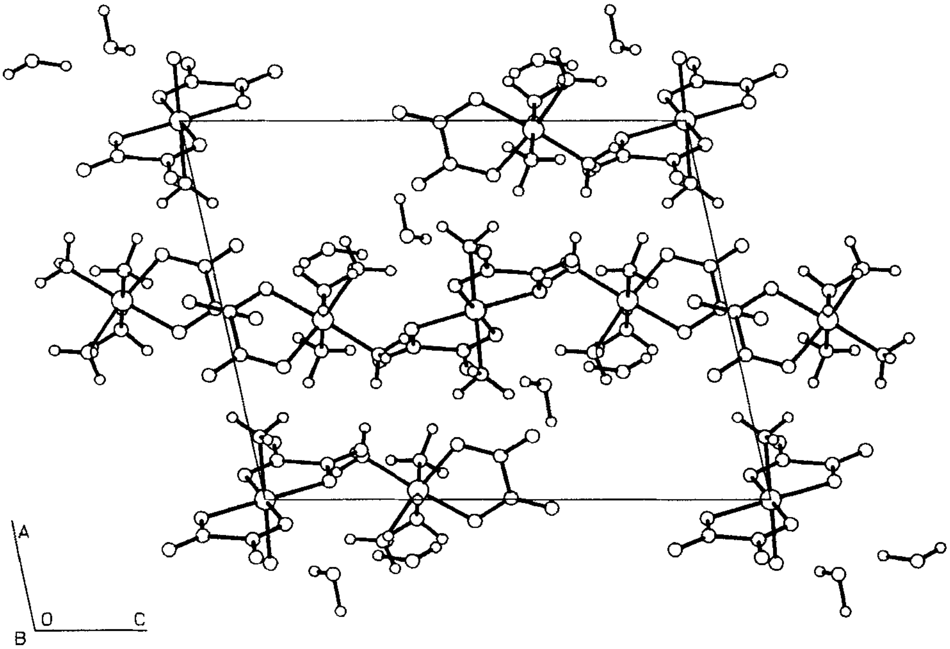

Figure 4 The packing mode of cations, anions and waters of crystallization in compound (II). This is a *b* axis projection. Beginning at 0,0,0, note the alternation of anion-cation-anion-cation.... along the *a* and *c* axes, as well as along $a = 1/2$. The Co cations and anions are hydrogen bonded to one another in strings, which, in turn, are linked by waters of crystallization.

Table 3 Positional parameters and estimated Standard Deviations for **I**.

Atom	*x/a*	*y/b*	*z/c*	$B(\text{Å}^2)$
Co	0.10484(3)	0.2500	0.18041(7)	1.603(6)
Cl1	-0.02536(6)	0.2500	-0.0383(1)	2.71(2)
Cl2	0.14743(4)	0.50121(6)	-0.34052(9)	2.53(1)
O1	0.0108(2)	0.2500	0.4067(5)	3.74(6)
N1	0.2173(2)	0.2500	0.3672(5)	2.36(5)
N2	0.1999(2)	0.2500	-0.0414(5)	2.62(6)
N3	0.1025(2)	0.4398(2)	0.1771(3)	2.40(4)
H1	0.2126	0.1748	0.4471	4.0*
H2	0.2757	0.2500	0.2940	4.0*
H4	0.2396	0.1748	-0.0329	4.0*
H5	0.1620	0.2500	-0.1608	4.0*
H7	0.1342	0.4745	0.0637	4.0*
H8	0.1347	0.4694	0.2949	4.0*
H9	0.0333	0.4662	0.1808	4.0*
H10	-0.0429	0.3183	0.3867	4.0*

* Hydrogen atoms were found experimentally and assigned fixed thermal parameters of 4.0 Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter-defined as: (4/3) * $[a^{2}*\beta_{11} + b^{2}*\beta_{22} + c^{2}*\beta_{33} + ab(\cos\gamma)*\beta_{12} + ac(\cos\beta)*\beta_{13} + bc(\cos\alpha)*\beta_{23}]$.

Table 4 Positional parameters and estimated standard deviations for **II**.

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Co1	0.5000	0.5000	0.5000	1.83(2)
Co2	0.02472(6)	0.2607(1)	0.30555(5)	1.39(1)
O1	0.5642(3)	0.7237(4)	0.4710(2)	1.97(8)
O2	0.5489(3)	0.5975(5)	0.6345(2)	2.49(9)
O3	0.6517(3)	0.9442(5)	0.5427(2)	2.7(1)
O4	0.6312(3)	0.8162(5)	0.7114(2)	2.50(9)
O5	0.1461(3)	0.3527(4)	0.4042(2)	1.72(8)
O6	-0.0565(3)	0.2054(4)	0.4041(2)	1.64(8)
O7	0.1695(3)	0.4145(5)	0.5559(2)	3.0(1)
O8	-0.0221(3)	0.2115(5)	0.5618(2)	3.1(1)
N1	0.3332(4)	0.6097(5)	0.4828(3)	1.9(1)
N2	0.1045(4)	0.0540(5)	0.3228(3)	1.7(1)
N3	-0.1093(4)	0.1719(5)	0.2149(3)	2.0(1)
N4	0.1152(4)	0.3171(5)	0.2109(3)	1.8(1)
N5	-0.0510(4)	0.4728(6)	0.2903(3)	2.0(1)
C1	0.6046(5)	0.8113(6)	0.5415(3)	1.6(1)
C2	0.5945(4)	0.7360(7)	0.6388(3)	1.8(1)
C3	0.1154(5)	0.3457(7)	0.4845(4)	1.8(1)
C4	0.0042(5)	0.2463(7)	0.4863(3)	1.9(1)
Ow1	0.6606(3)	0.3372(5)	0.2358(2)	2.8(1)
Ow2	0.6954(3)	0.1199(5)	0.3981(3)	3.4(1)
Hw1	0.6250	0.3046	0.1835	4*
Hw2	0.6464	0.2773	0.3007	4*
Hw3	0.6875	0.0546	0.4335	4*
Hw4	0.7929	0.1386	0.4003	4*
H1	0.2814	0.5578	0.4283	4*
H2	0.3409	0.7185	0.4680	4*
H3	0.2810	0.6103	0.5280	4*
H4	0.0705	-0.0120	0.3627	4*
H5	0.1886	0.0712	0.3524	4*
H6	0.1035	0.0000	0.2656	4*
H7	-0.1806	0.2152	0.2268	4*
H8	-0.1035	0.1933	0.1503	4*
H9	-0.1090	0.0571	0.2241	4*
H10	0.0727	0.2718	0.1531	4*
H11	0.1250	0.4453	0.1992	4*
H12	0.1906	0.2710	0.2293	4*
H13	0.0000	0.5566	0.3007	4*
H14	-0.1035	0.4775	0.3325	4*
H15	-0.0959	0.4780	0.2270	4*

* Hydrogen atoms were found experimentally and assigned fixed thermal parameters of 4.0 Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3) * [a^2{*}\beta_{11} + b^2{*}\beta_{22} + c^2{*}\beta_{33} + ab(\cos\gamma){*}\beta_{12} + ac(\cos\beta){*}\beta_{13} + bc(\cos\alpha){*}\beta_{23}]$.

be due to the fact that the oxalate anion reacts with the water medium to form protonated oxalato species ($C_2O_4H^-$) and OH^- anions which enter the coordination sphere. Thus, this reaction merits mechanistic and kinetic observation. The fact that the two NO_2 ligands can be displaced by oxalic acid is obvious from the composition of (II), which was obtained by the addition of excess oxalate and a smaller amount of NaCl. Moreover, in the Cr(III) series, compounds have been isolated[15] from mixtures of $[Cr(en)_2Cl_2]^+$ cations and oxalate, and which have been formulated as containing en, oxalato and OH ligands in the Cr(III) coordination

Table 5 Bond distances and angles for **I**.

A) Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	Cl1	2.272(1)	Co	O1	1.971(1)
Co	N1	1.954(1)	Co	N2	1.956(1)
Co	N3	1.959(1)	N1	H1	0.946(1)
N1	H2	0.920(1)	N2	H4	0.940(1)
N2	H5	0.948(1)	N3	H7	0.943(1)
N3	H8	0.952(1)	N3	H9	0.959(1)
O1	H10	1.013(1)			

B) Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl1	Co	O1	91.00(4)	Cl1	Co	N1	179.68(4)
Cl1	Co	N2	89.85(4)	Cl1	Co	N3	88.89(3)
O1	Co	N1	89.33(6)	O1	Co	N2	179.16(6)
O1	Co	N3	89.93(3)	N1	Co	N2	89.83(6)
N1	Co	N3	91.11(3)	N2	Co	N3	90.09(3)
Co	O1	H10	110.18(9)	Co	N1	H1	108.45(8)
Co	N1	H2	107.6(1)	Co	N2	H4	108.46(8)
Co	N2	H5	107.8(1)	Co	N3	H7	112.48(7)
Co	N3	H8	107.75(6)	Co	N3	H9	107.43(7)
H1	N1	H2	111.05(9)	H4	N2	H5	110.45(9)
H7	N3	H8	110.54(9)	H7	N3	H9	109.95(8)
H8	N3	H9	108.55(9)				

Table 6 Bond distances and angles for **II**.

A) Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co1	O1	2.072(2)	O4	C2	1.242(3)
Co1	O2	2.077(2)	O5	C3	1.286(3)
Co1	N1	2.079(2)	O6	C4	1.291(3)
Co2	O5	1.927(2)	O7	C3	1.229(3)
Co2	O6	1.919(2)	O8	C4	1.231(3)
Co2	N2	1.934(2)	C1	C2	1.571(3)
Co2	N3	1.941(2)	C3	C4	1.521(4)
Co2	N4	1.943(2)	Ow1	Hw1	0.826(2)
Co2	N5	1.953(2)	Ow2	Hw4	1.120(2)
O1	C1	1.260(3)	Ow2	Hw3	0.766(2)
O2	C2	1.258(3)	Ow1	Hw2	1.107(2)
O3	C1	1.225(3)			

B) Selected Hydrogen Bonds up to 2.1 Å (distances in Å, angles in degrees)

*Intramolecular**

O3	—	Hw3	1.947	Ow2	—	Hw3....O3	162.8
Ow2	—	Hw2	1.918	Ow1	—	Hw2....Ow2	149.4

*Intermolecular**

O1	—	H8	1.925	N3	—	H8.....O1	170.2	N3	at 1/2−*x*, 1/2+*y*, 1/2−*z*
O2	—	H6	2.039	N2	—	H6.....O2	162.8	N2	at 1/2+*x*, 1/2−*y*, 1/2+*z*
O4	—	H11	1.987	N4	—	H11....O4	164.6	N4	at 1/2+*x*, 1.5−*y*, 1/2+*z*
O6	—	Hw4	1.797	Ow2	—	Hw4....O6	170.0	Ow2	at −1+*x*, *y*, *z*
Ow1	—	H9	2.039	N3	—	H9.....Ow1	159.0	N3	at 1/2−*x*, 1/2+*y*, 1/2−*z*

C) Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Co1	O2	78.81(7)	H5	N2	H6	106.5(2)
O1	Co1	N1	86.46(8)	Co2	N3	H7	108.7(2)
O2	Co1	N1	89.96(8)	Co2	N3	H8	112.3(2)
O5	Co2	O6	85.80(7)	Co2	N3	H9	107.7(2)
O5	Co2	N2	90.57(8)	H7	N3	H8	110.3(2)
O5	Co2	N3	173.92(9)	H7	N3	H9	109.3(2)

Continue on next page

Table 6 *Continued.*

C) Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O5	Co2	N4	91.30(8)	H8	N3	H9	108.5(2)
O5	Co2	N5	87.66(9)	Co2	N4	H10	106.2(2)
O6	Co2	N2	88.92(8)	Co2	N4	H11	115.7(2)
O6	Co2	N3	88.70(8)	Co2	N4	H12	107.4(2)
O6	Co2	N4	176.85(9)	H10	N4	H11	107.4(2)
O6	Co2	N5	91.53(8)	H10	N4	H12	111.1(2)
N2	Co2	N3	91.91(9)	H11	N4	H12	109.1(2)
N2	Co2	N4	89.88(9)	Co2	N5	H13	115.0(2)
N2	Co2	N5	178.1(1)	Co2	N5	H14	107.0(2)
N3	Co2	N4	94.25(9)	Co2	N5	H15	106.6(2)
N3	Co2	N5	89.91(9)	H13	N5	H14	109.6(2)
N4	Co2	N5	89.58(9)	H13	N5	H15	108.9(2)
Co1	O1	C1	115.9(2)	H14	N5	H15	109.6(2)
Co1	O2	C2	115.3(2)	O1	C1	O3	128.0(3)
Co2	O5	C3	111.3(2)	O1	C1	C2	114.6(2)
Co2	O6	C4	112.1(2)	O3	C1	C2	117.5(3)
Co1	N1	H1	106.6(2)	O2	C2	O4	126.4(3)
Co1	N1	H2	108.7(2)	O2	C2	C1	115.4(2)
Co1	N1	H3	126.7(2)	O4	C2	C1	118.3(3)
H1	N1	H2	108.0(2)	O5	C3	O7	123.9(3)
H1	N1	H3	101.2(2)	O5	C3	C4	115.4(2)
H2	N1	H3	104.4(2)	O7	C3	C4	120.6(3)
Co2	N2	H4	110.6(2)	O6	C4	O8	125.2(3)
Co2	N2	H5	108.6(2)	O6	C4	C3	114.4(2)
Co2	N2	H6	113.1(2)	O8	C4	C3	120.4(3)
H4	N2	H5	108.1(2)	Hw1	Ow1	Hw2	120.2(2)
				Hw3	Ow2	Hw4	109.7(2)

D) Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
O2	Co1	O1	C1	2.0
N1	Co1	O1	C1	92.6
O1	Co1	O2	C2	- 1.4
N1	Co1	O2	C2	- 87.8
O6	Co2	O5	C3	- 4.3
N2	Co2	O5	C3	- 93.2
N3	Co2	O5	C3	20.9
N4	Co2	O5	C3	176.9
N5	Co2	O5	C3	87.4
O5	Co2	O6	C4	- 2.2
N2	Co2	O6	C4	88.4
N3	Co2	O6	C4	- 179.6
N4	Co2	O6	C4	20.8
N5	Co2	O6	C4	- 89.8
Co1	O1	C1	O3	176.6
Co1	O1	C1	C2	- 2.1
Co1	O2	C2	O4	- 179.2
Co1	O2	C2	C1	0.8
Co2	O5	C3	O7	- 170.1
Co2	O5	C3	C4	9.2
Co2	O6	C4	O8	- 172.9
Co2	O6	C4	C3	7.4
O1	C1	C2	O2	0.8
O1	C1	C2	O4	- 179.1
O3	C1	C2	O2	- 178.0
O3	C1	C2	O4	2.1
O5	C3	C4	O6	- 11.5
O5	C3	C4	O8	168.8
O7	C3	C4	O6	167.8
O7	C3	C4	O8	- 11.9

sphere. Thus ligand displacement followed by anation seems to be common, and readily observed, in the chemistry of both Cr(III) and Co(III) amines. These comments apply equally well to the isolation and formulation of (II), below.

Compound (II) contains the cation we were searching for; however, the excess of oxalate results in displacement of three ammonias as well as the two nitro ligands to form the charge compensating anions found herein. This species is historically interesting in that, in 1922, Riesenfeld and Klemm[16] reported isolating K[*trans*-$Co(NH_3)_2(ox)_2$] by the reaction of oxalate anions with Erdmann's salt, K[*trans*-$(NH_3)_4Co(NO_2)_4$], and claimed the product contained two NH_3 ligands *trans* to each other; however, at that time it was impossible to prove such a claim unambiguously. In view of our results with (II), we feel that, indeed this species was probably formed in the system described by them; moreover, it was probably not the only species present in their reaction medium — merely the most insoluble one, given the conditions they used. Such accidental isolation of mixed cation-anion pairs, both containing a common metal, has been noted before in the Cr(III) system[15] mentioned above, where $[Cr(en)_2ox][Cr(en)(ox)_2]\cdot 2H_2O$ crystals were isolated and their crystal structure determined. These authors remarked, that in their system, other products probably existed and that the ones they isolated were merely those which exceeded the solubility limit of certain potential combinations of cation-anion or were neutral species, such as $[Cr(en)(ox)(\mu_2\text{-}OH)_2Cr(en)(ox)]$.[15]

Finally, let us compare stereochemical data for the cation of (II) with compounds $[Co(NH_3)_4Ox]I\cdot H_2O$ (III) and $[Co(NH_3)_4Ox]NO_3\cdot H_2O$ (IV).[17] Despite the identical nature of the cations in (II), (III) and (IV), there is a distinct irregularity in the relationship between the axial (amines *trans* to one another) and basal plane Co-N distances (amines *trans* to oxalate oxygens). In (II) and (IV) the average value of the axial Co-N distances are a little longer than the basal ones, while in (III) the reverse is true. At the moment we are attributing this difference to the influence that the charge compensating anions have on the amine nitrogens of the cations. In (II) and (IV) the anions are powerful hydrogen bonding species which seem able to selectively weaken the Co-N bonds.This is not possible in the case of (III) since, by comparison with oxalate and nitrate, iodide is a very poor hydrogen bonding species. Thus, the nature of the counteranion seems to influence the inner sphere (Co-N) bonds in a way that it can counteract the traditional *trans* effect between the ligands in the coordination sphere. If this observation is indeed general, *trans* effects should best be measurable in compounds in which hydrogen bonding effects are reduced to a minimum.

Compound	Co-N(basal)	Co-N(axial)	Co-O(ox)*
(II) Cation	1.941(2)	1.934(2)	1.919(2)
	1.943(2)	1.953(2)	1.927(2)
(III)	1.989(4)	1.961(4)	1.889(3)
	1.967(4)	1.968(3)	1.907(3)
(IV)	1.952(2)	1.960(2)	1.902(1)
	1.963(2)	1.978(2)	1.899(1)Å

* Each Co-O distance in a given line is *trans* to the Co-N distance in the same line of the first column.

The oxalato C-C distances for the cation and anion of (II) are, respectively, 1.521(4) and 1.571(3) Å. The bonded-oxygen C-O distances are: cation, 1.286(3) and 1.291(3) Å; anion, 1.260(3) and 1.258(3) Å. Finally, the C-O distances of the non-ligating oxygens are: cation, 1.229(3) and 1.231(3) Å; anion, 1.225(3) and 1.242(3) Å.

In conclusion, we feel that our accidental discovery of three new [Co(III)amines] species in solutions containing oxalate makes the relevant cobalt chemistry similar with that observed earlier[15] for Cr(III) and that, in both cases, the identification of these compounds may help chemists working on the equilibria, mechanisms and kinetics of anation reactions in sorting out the details of these systems. It should be clear that Co(III) and Cr(III) share similar chemistry and ligand displacement reactions, which are independent of metal and of the nature of the amine; *e.g.*, monodentate -NH_3 or bidentate en. Finally, if its established later that our observations on the influence of the counteranion on the *trans* effect in solids is general, this study was well worth the effort for that observation alone.

Supplementary material

Anisotropic thermal parameters for (I) and (II) (2 pages), structure factor tables (I) and (II) (17 + 11 pages) are available from the authors upon request.

Acknowledgements

We thank the Robert A. Welch Foundation for support of this investigation through Grant E-594 and for Fellowships for J. Cetrullo and J. Myrczek. We also thank the US National Science Foundation for the funds used to purchase the diffractometer.

References

1. I. Bernal and J. Cetrullo, *Struct. Chem.*, **1**, 235 (1990).
2. Y. Shibata and T.J. Maruki, *Chem. Soc. Japan*, **37**, 1142 (1916).
3. Y. Komiyama, *Bull. Chem. Soc. Japan*, **30**, 13 (1957).
4. I. Bernal and J. Cetrullo, *J. Coord. Chem.*, **20**, 247 (1989).
5. M. Ito, and M. Shibata, *Chem. Lett.*, **4**, 375 (1975).
6. H. Grubitsch, "*Anorganisch-präparative Chemie*", (Springer-Verlag, Vienna, 1950), p. 447.
7. X. Liang, S. Suwanrumpha and R.B. Freas, *Inorg. Chem.*, **30**, 652 (1991).
8. Galbraith Laboratories, Inc., 2323 Sycamore Dr., Knoxville, Tenn., 37921.
9. TEXRAY-230 is a modification of the SDP-Plus[10] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3200 Research Forest Dr., The Woodlands, TX 77386, U.S.A., for use with their automation of the CAD-4 diffractometer.
10. SDP-Plus is the Enraf-Nonius Corporation X-ray diffraction data processing programs distributed by B.A. Frenz and Associates, 1140 East Harvey Road, College Station, TX 77840, U.S.A.
11. R.B. Roof, "*A Theoretical Extension of the Reduced Cell Concept in Crystallography*", Report LA-4038, Los Alamos Scientific Laboratory (1969).
12. D.T. Cromer and J.T. Waber "*International Tables for X-Ray Crystallography*", (Kynoch Press, Birmingham, England, 1975) Vol. IV, Tables 2.2.8 and 2.3.1 (respectively, for the scattering factor curves and the anomalous dispersion values).
13. I. Bernal, *J. Coord. Chem.*, **15**, 337 (1987).
14. X. Solans, M. Font-Altaba, J.L. Brianso, A. Solans, J. Casabo and J. Ribas, *Struct. Commun.*, **11**, 1199 (1982).
15. J.W. Lethbridge, L.S. Dent Glasser, and H.F.W. Taylor, *J. Chem. Soc., (A).*, 1862 (1970).
16. F.H. Riesenfeld and R. Klemm, *Z. anorg. Chem.*, **124**, 1 (1922).
17. I. Bernal and J. Cetrullo, *Struct. Chem.*, **1**, 227 (1990).