

# Complexes of the Trioxodinitrate Anion: Synthesis and Characterization of [Zn<sup>II</sup>(bipy)(H<sub>2</sub>O)(N<sub>2</sub>O<sub>3</sub>)] and [Co<sup>II</sup>(bipy)<sub>2</sub>(N<sub>2</sub>O<sub>3</sub>)]

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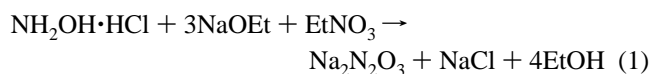
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The first two complexes of the trioxodinitrate anion were prepared by reaction of Zn(bipy)Cl<sub>2</sub>·1.5H<sub>2</sub>O (1·1.5H<sub>2</sub>O) with Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O in water to produce Zn<sup>II</sup>(bipy)(H<sub>2</sub>O)(N<sub>2</sub>O<sub>3</sub>) (2) and an analogous reaction of Co(bipy)<sub>2</sub>Cl<sub>2</sub>·2.5H<sub>2</sub>O (3·2.5H<sub>2</sub>O) to produce Co<sup>II</sup>(bipy)<sub>2</sub>(N<sub>2</sub>O<sub>3</sub>) (4). Both complexes are air-sensitive and crystallize in the monoclinic space group *P*2<sub>1</sub>/*n*. For 2·H<sub>2</sub>O *T* = 24–26 °C, *Z* = 4, *a* = 7.7595(6) Å, *b* = 9.4798(7) Å, *c* = 17.197(1) Å, β = 98.142(7)°, and *V* = 1252.3(2) Å<sup>3</sup>. The final residuals were *R*1 = 0.0452, *wR*2 = 0.1172, and quality-of-fit = 1.057. The final model consisted of the main structure and a minor, 4% disordered component. For 4·4H<sub>2</sub>O *T* = –123 °C, *Z* = 4, *a* = 9.0950(9) Å, *b* = 17.924(3) Å, *c* = 13.695(2) Å, β = 90.32(1)°, and *V* = 2232.5(6) Å<sup>3</sup>. The final least-squares residuals were *R*1 = 0.0859, *wR*2 = 0.1975, and quality-of-fit = 0.917. A network of hydrogen bonds involving the crystal water molecules and the coordinated trioxodinitrate anion was found in each case; in 4, a series of fused four- and eight-membered rings were found to be a dominant feature in the extended structure. The structural data and the IR spectrum indicate that the N–N bond of trioxodinitrate, 1.264(5) Å in the free anion, is longer for the coordinated anion (1.280(5) Å in 2 and 1.333(11) Å in 4).

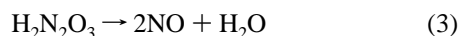
## Introduction

The trioxodinitrate anion was first prepared in 1896 as the sodium salt, Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (Angeli's salt). The compound is also known as sodium hyponitrate, sodium trioxodinitrate(II), and sodium oxyhyponitrite. It can be prepared in the laboratory by reduction of an alkyl nitrate with hydroxylamine as shown in reaction 1:<sup>1</sup>

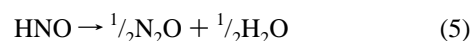
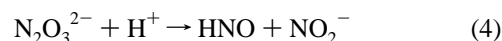


The structure of the monohydrate was determined by X-ray diffraction, and it was found to consist of a planar anion with a nitrogen to nitrogen distance consistent with a double bond.<sup>2</sup>

The salt decomposes slowly if the pH is strongly basic according to eq 2; in acid media it decomposes rapidly with a different stoichiometry as shown in eq 3:<sup>3,4</sup>



Reaction 3, however, is not a simple dehydration as there is evidence for a more complicated mechanism, and nitroxyl has been suggested as an intermediate in reaction 2 as shown in reactions 4 and 5.<sup>5,6</sup>



We have been studying the coordination chemistry of the trioxodinitrate anion, with the hope of shedding light on some of the questions that have arisen with regard to its behavior. Coordinated N<sub>2</sub>O<sub>3</sub> species have been postulated during the catalytic reduction of nitrogen oxides on Cu- or Co-exchanged ZSM-5 zeolites.<sup>7</sup> Another question involves whether the trioxodinitrate species occurs as an intermediate in the denitrification process during the reduction of nitrite to dinitrogen monoxide.<sup>8–10</sup> The highest oxidation state nitrogen oxoanion that contains a N=N bond is trioxodinitrate, and it is conceivable that two nitrogen atoms (from NO<sub>2</sub>) become bonded at this oxidation level in some of the reductions. To the best of our knowledge, there are no reports of structurally characterized trioxodinitrate complexes, and we considered it important to explore its coordination chemistry for providing much needed model compounds. The preparation of transition metal compounds with the coordinated trioxodinitrate anion might then be useful in understanding the mechanism of formation of multiple N to N bonds that is the common factor in the above-mentioned processes.

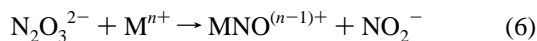
In order to avoid oxidation of N<sub>2</sub>O<sub>3</sub><sup>2-</sup> to NO<sub>2</sub><sup>-</sup> we chose as an entry point to our research reactions with Zn<sup>2+</sup> and Co<sup>2+</sup>. The complexes Zn(bipy)Cl<sub>2</sub> and Co(bipy)<sub>2</sub>Cl<sub>2</sub> were used as convenient starting materials for reaction with Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub> in order to determine how trioxodinitrate would bind to the metal atoms. The vibrational spectra of nitrogen oxospecies has been

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1997.

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reviewed, and it provided a convenient diagnostic tool for the characterization of the compounds.<sup>11</sup> Another question we sought to answer was whether, in the presence of metal cations, a reaction such as



could become a decomposition route with  $\text{NO}_2^-$  being formed, not as a result of oxidation but from a Lewis acid catalyzed disproportionation in which the metal cation has a role similar to that of  $\text{H}^+$  in reaction 4 (this did not in fact happen under the conditions that we explored). Our attempts to use  $\text{N}_2\text{O}_3^{2-}$  as a ligand proved fruitful, and we report here the synthesis and characterization of the first transition metal complexes of the trioxodinitrate anion.

## Experimental Section

Where noted, reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques.<sup>12</sup> All reagents and solvents were reagent grade. Solvents were purified by reflux and distillation under nitrogen in the presence of the appropriate drying agent.

Infrared spectra were measured using a Shimadzu FTIR-8101 Fourier transform spectrophotometer. UV-visible spectra were recorded in a Shimadzu UV-160 spectrophotometer. Zinc and cobalt analyses were carried out by atomic absorption in a Perkin-Elmer 3300 spectrophotometer. Magnetic susceptibilities were measured in a Johnson-Mathey MSB-1 balance. The ligand 2,2'-bipyridine was analyzed spectrophotometrically at 301 nm after we dissolved the compounds in 10%  $\text{H}_2\text{SO}_4$ . Chloride was determined volumetrically in the Zn compound by Mohr's method. For the Co compound, chloride was measured by precipitation potentiometry with standard  $\text{AgNO}_3$  solution, using a silver indicator electrode in an acidic ( $\text{HNO}_3$ ) medium and 0.5 g of  $\text{Ba}(\text{NO}_3)_2/100$  mL. Nitrogen analysis was performed in a Perkin-Elmer Series II, model 2410 nitrogen analyzer.

Sodium trioxodinitrate monohydrate,  $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , was prepared using the standard literature methods, purified by recrystallization from ethanol-water, and stored under nitrogen after preparation.<sup>12</sup>

**(Bipyridine)dichlorozinc(II),  $\text{Zn}(\text{bipy})\text{Cl}_2$ , 1.** A solution of  $\text{ZnCl}_2$  (1.28 g, 9.4 mmol) in methanol (5 mL) was prepared in a 50 mL Erlenmeyer flask which was covered by aluminum foil. To this was slowly added a solution of bipy (2.91 g, 18.6 mmol) in methanol (7 mL). The reaction mixture was stirred in the dark for 2 days, and a white precipitate formed. The mixture was cooled in ice; the solid was separated by filtration and washed with 1:1 MeOH-ether (5 mL) and ether (5 mL). The solid was recrystallized from water, and a white crystalline solid was obtained. The yield was 1.3 g (44%). Anal. Calcd for  $\text{Zn}(\text{bipy})\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$  (1·1.5 $\text{H}_2\text{O}$ ): Zn, 20.46; bipy, 48.88; Cl, 22.19. Found: Zn, 20.2; bipy, 48.6; Cl, 22.9. IR spectrum,  $\text{cm}^{-1}$  (KBr): 3050 s, 1607 s, 1599 s, 1541 w, 1509 w, 1493 m, 1474 s, 1445 s, 1318 m, 1252 w, 1159 m, 1063 w, 1019 s, 779 s, 739 s, 733 m, 652 w.

**Aqua(bipyridine)(trioxodinitrate)zinc(II),  $\text{Zn}(\text{bipy})(\text{H}_2\text{O})(\text{N}_2\text{O}_3)$ , 2.** All operations in this synthesis were carried out under  $\text{N}_2$ . A solution of  $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (0.266 g, 1.90 mmol) in water (2 mL) was slowly added to a solution of  $\text{Zn}(\text{bipy})\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$  (0.602 g, 1.86 mmol) in deoxygenated water (12 mL). The resulting mixture was stirred for 3 min, and a slightly yellow turbidity appeared. The mixture was then stored at 0 °C for 1 h, and a white precipitate formed. The solid was separated by filtration, washed with EtOH (3 mL) and ether (10 mL), and dried. The yield was 0.32 g (52%). The product is very hygroscopic, and even though it can be prepared or handled in air, it is best kept under  $\text{N}_2$ . In order to grow crystals for structure determination, a solution of  $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (0.10 g, 0.70 mmol) in water (5 mL) was slowly added to a solution of  $\text{Zn}(\text{bipy})\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$  (0.30 g, 0.70 mmol) in deoxygenated water (15 mL) and MeOH (10 mL). Appropriate crystals formed after the resulting mixture was stored at 5 °C for 1 day. Anal. Calcd for  $\text{Zn}(\text{bipy})(\text{H}_2\text{O})(\text{N}_2\text{O}_3) \cdot 1.5\text{H}_2\text{O}$  (2·1.5 $\text{H}_2\text{O}$ ): Zn, 19.08; bipy, 45.58; N, 16.35. Found: Zn, 18.9; bipy,

45.8; N, 16.0. IR spectrum,  $\text{cm}^{-1}$  (KBr): 3030 m, 1601 s, 1479 m, 1443 s, 1385 m, 1275 s, 1071 s, 1019 m, 961 m, 771 s, 740 m.

**Bis(bipyridine)dichlorocobalt(II),  $\text{Co}(\text{bipy})_2\text{Cl}_2$ , 3.** Under a  $\text{N}_2$  atmosphere a solution of bipy (3.52 g, 22.5 mmol) in MeOH (15 mL) was added with stirring to a blue solution of anhydrous  $\text{CoCl}_2$  (1.47 g, 11.3 mmol) in methanol (15 mL). The resulting deep-red solution produced red crystals after storage at -12 °C for 1 day. The product was separated by filtration, washed with cold MeOH, and dried under  $\text{N}_2$ . The yield was 4.5 g (8.3 mmol). Anal. Calcd for  $\text{Co}(\text{bipy})_2\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$  (3·2.5 $\text{H}_2\text{O}$ ): Co, 12.09; bipy, 64.11; N, 11.50; Cl, 14.55. Found: Co, 12.1; bipy, 64.4; N, 11.5; Cl, 14.6. Magnetic moment: 4.58  $\mu_B$ . IR spectrum,  $\text{cm}^{-1}$  (KBr): 1597 s, 1568 w, 1470 m, 1439 s, 1402 m, 1314 m, 1017 s, 774 s, 735 m, 650 w; using dry Nujol a weak band was observed at 3440  $\text{cm}^{-1}$ .

**Bis(bipyridine)(trioxodinitrate)cobalt(II),  $\text{Co}(\text{bipy})_2\text{N}_2\text{O}_3$ , 4.** Solid  $\text{Co}(\text{bipy})_2\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$  (1.26 g, 2.59 mmol) and  $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (0.573 g, 2.92 mmol) were dissolved in water (15 mL) under a  $\text{N}_2$  atmosphere. After a few seconds of stirring orange microcrystals appeared. Stirring was continued for a few more minutes, and the product was isolated by filtration, washed with cold water, and dried under  $\text{N}_2$ . The yield of the tetrahydrate was 0.53 g (41%). The crystals of 4·4 $\text{H}_2\text{O}$  lose water of crystallization very easily, and in order to obtain good analysis data they had to be dried under a dynamic vacuum for 2 h. Crystals suitable for structure determination were prepared by repeating the above procedure with the same amount of water but using 0.480 g, 1.09 mmol, and 0.163 g, 0.833 mmol, of the above reagents, respectively. After the first microcrystals formed, water was added until the solid redissolved. The orange solution was stored at 3 °C for 1 day, and large, orange single crystals formed. They were extremely prone to solvent loss and had to be kept in contact with a portion of the mother solution at all times. Anal. Calcd for  $\text{Co}(\text{bipy})_2\text{N}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$  (4·2.5 $\text{H}_2\text{O}$ ): Co, 11.97; bipy 63.44; N, 17.07. Found: Co, 12.0; bipy, 63.4; N, 17.1. Magnetic moment: 3.99  $\mu_B$ . IR spectrum,  $\text{cm}^{-1}$  (KBr): 1601 s, 1570 w, 1472 m, 1441 s, 1383 s, 1314 m, 1269 s, 1161 m, 1055 s, 1044 m, 1017 m, 922 m, 816 m, 774 s, 733 m; using dry Nujol water bands at 3360 s and 1638 m appear. Visible spectrum in deoxygenated water  $\lambda_{\text{max}}$ : 586 (sh) and 638 nm ( $\epsilon = 20 \text{ M}^{-1} \text{ cm}^{-1}$ ).

**Crystal Data for  $\text{Zn}(\text{bipy})(\text{H}_2\text{O})(\text{N}_2\text{O}_3)$ .** A flat, colorless crystal was mounted at the end of a glass fiber and covered with epoxy. Geometric and intensity data were taken from this crystal using routine procedures on a four-circle diffractometer.<sup>13</sup> Axial photos of the *a*-, *b*-, and *c*-axes, as well as [111], were used to verify the lattice constants and Laue group. During intensity data collection, a variable scan speed was used in which weaker reflections, as determined in a first scan, were measured at a slower speed in a final scan than were stronger reflections. The very weakest reflections were measured at the slowest speed: that is, no datum was skipped. The intensities of three monitor reflections were checked after each three hours of X-ray exposure, and the orientation of the crystal was checked after every 500 data measurements. Eleven  $\psi$ -scans were used as the basis of an absorption correction.<sup>14</sup> Seven of these were of reflections with bisecting-position Eulerian angle  $\chi$  near 90°, and the other four consisted of two pairs of symmetry-equivalent reflections with bisecting-position  $\chi$  values between 20 and 60°.

All non-hydrogen atoms of the complex  $\text{Zn}(\text{bipy})(\text{N}_2\text{O}_3)(\text{H}_2\text{O})$ , as well as the oxygen atom of an unligated water molecule, were located by an algorithm<sup>14</sup> that applies Patterson map analysis, difference direct methods, and peaklist optimization. All but one of the hydrogen atoms were located in a difference Fourier map at the end of anisotropic convergence of a model consisting of the non-hydrogen atoms. The structure was refined to  $F_o^2$ , and all data were used in the refinement.<sup>15</sup>

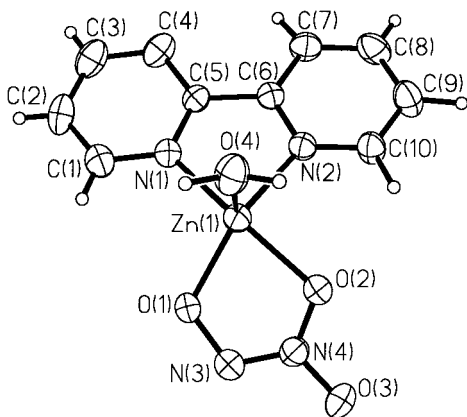
Our first attempts at refining the structure led to instability, which required the application of restraints in order to achieve convergence.

(13) Diffractometer control program: CAD4-PC Version 1.5c, Delft Instruments X-ray Diffraction bv, Delft, The Netherlands, 1994.

(14) (a) Data were processed on a Local Area VAXcluster (VMS V5.5-2), by the program XCAD4B (K. Harms, private communication) and with the commercial package SHELXTL-PLUS Release 4.21/V: Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990. (b) Direct-methods calculations were done on a Hewlett-Packard Series 9000 computer, Model 715/50 (HP-UX V9.01), with the program SHELXS-96, Beta release of March 1996. (c) SHELXS-96, FORTRAN Program for Crystal Structure Determination; George M. Sheldrick, 1996.

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**Figure 1.** Drawing of one molecule of complex **2** showing the atom-naming scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids. The hydrogen atom attached to C(4) was not included in the structural model, as described in the text and Supporting Information.

This refinement gave  $R1 = 0.0548$ ,  $wR2 = 0.1458$ , and quality-of-fit = 1.086. A difference Fourier map at this point revealed a single peak greater than  $1.0 \text{ e}/\text{\AA}^3$  ( $\Delta\rho = 1.82 \text{ e}/\text{\AA}^3$ ), which was located at the distal side of the bipyridyl ligand, in a position roughly opposite to the position of the zinc atom of the complex. This raised the possibility that there was a second, minor disordered component to the structure, with the bipy ligand flipped so that its nitrogen atoms were roughly—but not exactly—at the positions occupied by atoms C(4) and C(7) of the major-component bipy ligand (see Figure 1 for the atom-naming scheme). Full details of the treatment of this apparent disorder are given in the Supporting Information, and only a summary of the final refinement is given here. Briefly, four disordered models and one twin model were tested for the evident minor component, which had about 4% population in the structure. In the final model were included all atoms of the principal component, except for one hydrogen atom which was overlapped with a non-hydrogen atom of the secondary component. The minor-component zinc atom and the non-hydrogen atoms of the secondary bipy ligand were included in the structural model. For the main component, all hydrogens were treated as riding atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. All non-hydrogen atoms of the main structure were refined with anisotropic displacement parameters. With the final structural model, consisting of the main structure and a minor disorder, the value of  $wR2$  dropped by nearly three percentage points with respect to the undisordered model. The final residuals are given in Table 1.

**Crystal Data for  $\text{Co}(\text{bipy})_2(\text{N}_2\text{O}_3)$ .** Blood-red crystals of  $[\text{Co}(\text{bipy})_2(\text{N}_2\text{O}_3)] \cdot 4\text{H}_2\text{O}$  were transported from the University of Costa Rica to the University of Zaragoza in a sealed glass ampoule, in the presence of their mother liquid. It was observed before the ampoule was opened that many of the crystals had suffered physical decomposition during transport, although there remained some crystals, with what was judged to be good appearance, in the midst of a lighter colored, flocculent precipitate. Shortly after the ampoule was opened, a quantity of red-orange platelike crystals precipitated. Five of the original red crystals were examined on the diffractometer before one with what were considered to be acceptable scattering properties was found. Each of the crystals examined was covered with lithium grease while still in the presence of its mother liquid, attached to the end of a quartz fiber using just the same grease, and rapidly transferred to the nitrogen gas cold stream of the diffractometer. The crystals were at no time exposed to air in the absence of their mother liquid, unless already completely covered with lithium grease.

After the initial indexing of the cell for the crystal used for data collection, axial photographs of  $a$ ,  $b$ ,  $c$ , and  $[111]$  were used to verify the lattice repeats and Laue group. Scan parameters for data collection were chosen on the basis of two-dimensional ( $\omega$ - $\theta$ ) plots of 25

**Table 1.** Crystallographic Data for Complex **2**· $\text{H}_2\text{O}$  and Complex **4**· $4\text{H}_2\text{O}$

	complex <b>2</b> · $\text{H}_2\text{O}$	complex <b>4</b> · $4\text{H}_2\text{O}$
empirical formula	$\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_5\text{Zn}$	$\text{C}_{20}\text{H}_{24}\text{N}_8\text{O}_7\text{Co}$
formula weight	333.61	519.38
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
$a$ , $\text{\AA}$	7.7595(6)	9.0950(9)
$b$ , $\text{\AA}$	9.4798(7)	17.924(3)
$c$ , $\text{\AA}$	17.197(1)	13.695(2)
$\alpha$ , deg	90	90
$\beta$ , deg	98.142(7)	90.320(10)
$\gamma$ , deg	90	90
$V$ , $\text{\AA}^3$	1252.3(2)	2232.5(6)
$Z$	4	4
$d_{\text{calcd}}$ , $\text{g}/\text{cm}^3$	1.770	1.545
crystal size, $\text{mm}^3$	$0.29 \times 0.26 \times 0.11$	$0.28 \times 0.16 \times 0.16$
$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	19.88	8.24
radiation (graphite monochromated)	Mo $\text{K}\alpha$ ( $\lambda_{\text{Mo}} = 0.71073 \text{ \AA}$ )	Mo $\text{K}\alpha$ ( $\lambda_{\text{Co}} = 0.71073 \text{ \AA}$ )
temp $^\circ\text{C}$	$24\text{--}26 \pm 1$	$-123 \pm 1$
$wR2^a$	0.1172	0.1975
$R1^b$	0.0452 (for $F_o^2 \geq 2 \cdot \sigma(F_o^2)$ )	0.0859 (for $F_o^2 \geq 2 \cdot \sigma(F_o^2)$ )

$$^a wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}. \quad ^b R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

reflections.<sup>13</sup> In a first shell of data, to  $38.0^\circ 2\theta$ , the weakest data were gathered at the slowest scan speed. Because of a rapid drop-off of scattered intensity with scattering angle, for a second shell of data ( $37.9\text{--}47.0^\circ 2\theta$ ), final scans were not performed for any reflection that failed to produce  $I/\sigma(I) > 0.05$  in a preliminary scan done at  $3.9^\circ/\text{min}$  in  $\omega$ . Toward the end of the second shell, the preliminary scan was slowed to  $2.6^\circ/\text{min}$  in  $\omega$ . During the collection of the second shell, a power failure of about 10 min duration caused the crystal to be left at room temperature for that time. The monitor reflections that were being used to follow crystal and instrument stability did not show any significant changes in intensity after the power failure. There was an irregular variation, which reached as much as 16%, in one of the intensity standards during the course of data collection, but the other two standards did not show such large changes. During data reduction the data were smoothed according to the average variation of the standards. Absorption corrections were based on  $\psi$ -scans of 11 reflections, seven of which had Eulerian angle  $\chi$  near  $90^\circ$ .<sup>14</sup> The other four reflections used for this purpose had bisecting-position  $\chi$  values between  $25$  and  $65^\circ$ .

The structure was solved by direct methods and refined by full-matrix least-squares methods.<sup>15</sup> After refinement of the parameters of the non-hydrogen atoms, some peaks corresponding to hydrogen atoms of the bipy groups were seen in difference maps; nonetheless, all of the hydrogen atoms of the two bipy ligands were added to the model at calculated positions and refined as riding atoms, with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent carbon atoms. Four independent uncoordinated water molecules were found in the asymmetric unit, and none of the hydrogen atoms of these were located. In the final refinement, all non-hydrogen atoms in the asymmetric unit were refined with anisotropic displacement parameters. The structure was refined to  $F_o^2$ , and all data with non-negative intensities were used in the refinement.

The refinement produced a rather high value for the unweighted residual  $R1$ , which we attribute to the unusual weakness of the diffraction pattern at higher scattering angles. The higher angle data, which we had observed to be systematically markedly weak and resistant to efforts to attain better measurements by lengthening the measuring time, were more poorly fitted in the least-squares refinement than were the lower angle data. We observed that the residuals could be lowered significantly by using an upper resolution cutoff. The result reported here is based on the refinement with all positive data, with no resolution cutoff.

## Results and Discussion

**Syntheses of the Complexes.** The starting material for the synthesis of the Zn complex,  $\text{Zn}(\text{bipy})\text{Cl}_2$ , was prepared by a

(15) (a) Refinement was carried out on the Hewlett-Packard Series 9000 computer, with the program *SHELXL-96*, Beta release of March 1996. (b) *SHELXL-96*, FORTRAN Program for Crystal Structure Refinement; George M. Sheldrick, 1996.

reaction which afforded initially a mixture of substances. The principal product was isolated by recrystallization from water as a white crystalline solid with good analysis data. The ratio of bipy to  $\text{ZnCl}_2$  in the reaction varied from 1:1 to 2:1, but this only affected the yield and not the identity of the isolated product. Water was evident from the IR spectrum, and the material was also found to be hygroscopic. Interestingly, the reaction had to be carried out in the absence of light, otherwise the reaction mixture turned red and the product was isolated as pink crystals. There is a report of the crystal structure of the same compound, which forms pink crystals. It was prepared by oxidation of a zinc anode in contact with a solution of bipy and tetraethylammonium chloride in acetonitrile.<sup>16</sup> Unfortunately, this method generated a mixture of products from which a single crystal was selected for structure determination and was not suitable for preparing the compound for synthetic purposes.

Reaction of 1 equiv of  $\text{Zn}(\text{bipy})\text{Cl}_2$  with  $\text{Na}_2\text{N}_2\text{O}_3$  in water quickly produced a white, very insoluble, microcrystalline solid which showed bands characteristic of trioxodinitrate at 1443, 1275, 1071, and  $961\text{ cm}^{-1}$  in the IR spectrum. In the sodium salt the corresponding frequencies, in  $\text{cm}^{-1}$ , were observed at 1400 ( $\text{NO}_2$  asymmetric stretching); 1280 ( $\text{NO}_2$  symmetric stretching); 1120, 1100 (N–N stretching); 980, 970 (N–O stretching). Absence of chloride ions was demonstrated by chemical analysis, and an IR spectrum in dry Nujol provided evidence for the presence of water. Chemical analysis suggested the formula of  $\text{Zn}(\text{bipy})(\text{N}_2\text{O}_3)(\text{H}_2\text{O})_2$ , and an X-ray structure determination was necessary to establish if one or two water molecules were bound to the metal atom. Crystallization times longer than 3 days were avoided due to the danger of decomposition of trioxodinitrate in solution.

A literature search for a cobalt compound with a similar structure to the Zn starting material indicated  $\text{Co}(\text{bipy})_2\text{Cl}_2$  as a convenient complex for ligand exchange.<sup>17</sup> We modified the reported synthetic procedure and obtained the compound with good yield and good analytical data. A similar reaction with 1 equiv of trioxodinitrate produced orange crystals that also showed in the IR spectrum the characteristic stretching bands of the anion. As mentioned in the Experimental Section, the crystals lose solvent water very easily and disintegrate in seconds once they are exposed to air or  $\text{N}_2$ . All data indicated the presence of unligated water molecules, and we expected to find the  $\text{N}_2\text{O}_3^{2-}$  anion to be again chelating and occupying the two positions left vacant by the two bipy ligands. The magnetic moments of both the starting material and of the trioxodinitrate complex are consistent with high-spin  $\text{Co}^{\text{II}}$ , and as expected are higher than the spin-only value of  $3.87\ \mu_{\text{B}}$  although they are in the low range for most reported  $\text{Co}^{\text{II}}$  compounds.<sup>18</sup> The electronic spectrum of complex **4** has a shoulder at  $17\ 100\text{ cm}^{-1}$  and a maximum at  $15\ 700\text{ cm}^{-1}$  ( $\epsilon = 20\ \text{M}^{-1}\text{ cm}^{-1}$ ) which can be assigned, on the basis of their energies and intensities, to the  ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}$  and the  ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$  transitions.<sup>18–20</sup> The  ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$  band is expected to fall in the near-IR and was not observed.<sup>18</sup>

#### Crystal Structure of the Complex $\text{Zn}(\text{bipy})(\text{H}_2\text{O})(\text{N}_2\text{O}_3)$ .

Packing in the extended structure is dominated by a division into wide slabs containing the ligated bipyridyl groups and narrower zones containing the hydrophilic parts of the structure—the zinc atom of the complex, the  $\text{N}_2\text{O}_3$  ligand, and

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) and Their Estimated Standard Deviations for Complex **2**<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Zn(1)	2076(1)	480(1)	1545(1)	34(1)
N(1)	1863(5)	1391(4)	418(2)	34(1)
N(2)	2651(5)	−1226(4)	858(2)	32(1)
C(1)	1403(7)	2738(5)	233(3)	45(1)
C(2)	1459(7)	3276(5)	−501(3)	48(1)
C(3)	2068(7)	2444(5)	−1057(3)	49(1)
C(4)	2536(6)	1054(5)	−887(3)	42(1)
C(5)	2385(5)	567(4)	−135(2)	29(1)
C(6)	2790(5)	−923(4)	106(2)	28(1)
C(7)	3256(6)	−1941(5)	−401(3)	39(1)
C(8)	3587(7)	−3293(5)	−116(3)	46(1)
C(9)	3441(7)	−3595(5)	652(3)	48(1)
C(10)	2958(7)	−2544(5)	1121(3)	39(1)
O(1)	158(4)	1511(3)	1929(2)	40(1)
O(2)	1439(5)	−841(4)	2389(2)	52(1)
O(3)	−604(5)	−1198(3)	3133(2)	46(1)
N(3)	−669(5)	797(4)	2450(2)	39(1)
N(4)	51(5)	−389(4)	2650(2)	33(1)
O(4)	4473(4)	1094(4)	1979(2)	45(1)
O(5)	5859(5)	−699(3)	3078(2)	54(1)

<sup>a</sup> The equivalent isotropic displacement parameter,  $U_{\text{eq}}$ , is calculated as  $U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i a_j^* a_j^* a_i^*$ .

the ligated and unligated water molecules. The bipy ligand of the complex lies in a plane roughly perpendicular to the crystallographic *x*-axis, and the bipyridyl groups of adjacent molecules related by crystallographic centers of symmetry are stacked along the *x*-direction. The disposition of the molecules with respect to the centers of symmetry is not perfectly symmetrical, so that there are two distinct stacking distances between adjacent bipy moieties, 3.55 and 3.61 Å. The hydrophobic region is extended by van der Waals' interactions between adjacent molecules in a second dimension—parallel to the crystallographic *y*-axis, to give a slablike arrangement in a plane roughly perpendicular to the *z*-axis. Between the hydrophobic regions lie thinner platelike hydrophilic zones. In the latter, stronger intermolecular interactions are found, in the form of hydrogen bonds. There are four crystallographically independent hydrogen bonds, donated by the four independent water hydrogen atoms—two each on the ligated and unligated water molecules.

The central zinc atom is pentacoordinated by the two chelating ligands and by one water (Figure 1). The chelate bite angles at zinc (L–Zn–L) are  $78.2(1)^\circ$  for  $\text{N}_2\text{O}_3$  and  $78.0(1)^\circ$  for bipy (Table 3). The coordination shell has a distorted square pyramidal geometry, with the ligated atoms of the two chelate ligands (O(1), O(2), N(1), and N(2)) forming the base of the pyramid. The mean deviation of these four atoms from their best plane is 0.10 Å. The zinc atom lies 0.525(2) Å out of this plane, displaced toward the apical water oxygen atom, O(4). The Zn(1)–O(4) bond makes an angle of  $7.5^\circ$  with the normal to the basal plane. Since the compounds reported here are to our knowledge the first in which  $\text{N}_2\text{O}_3$  is coordinated to a d-block element, we do not have a basis for comparison of the M–L distances involving the trioxodinitrate ligand, except between the present two compounds. The Zn(1)–N(1) and Zn(1)–N(2) distances, 2.107(4) and 2.088(3) Å, respectively, are in the range expected (Tables 2 and 3).

**Crystal Structure of the Complex  $\text{Co}(\text{bipy})_2(\text{N}_2\text{O}_3)$ .** A drawing of one molecule of the complex  $[\text{Co}(\text{bipy})_2(\text{N}_2\text{O}_3)]$  is shown in Figure 2, which also indicates the atom-naming scheme (Table 4). The coordination shell about cobalt has the shape of an octahedron with rhombic distortion caused by the presence of the three chelating ligands. The complex as a whole has nearly rigorous 2-fold symmetry, with the 2-fold axis bisecting the O(1)–Co(1)–O(2) angle. The inequivalence of

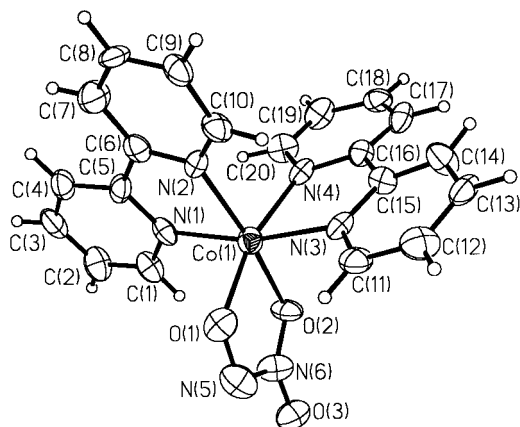
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**Figure 2.** Thermal ellipsoid plot of one molecule of complex **4** showing the atom-naming scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Complex **2**

Distances	
Zn(1)–O(1)	1.970(3)
Zn(1)–O(4)	1.990(3)
Zn(1)–O(2)	2.031(3)
Zn(1)–N(2)	2.088(3)
Zn(1)–N(1)	2.107(4)
N(1)–C(5)	1.338(5)
N(1)–C(1)	1.352(6)
N(2)–C(10)	1.339(5)
N(2)–C(6)	1.343(5)
O(1)–N(3)	1.355(5)
O(2)–N(4)	1.296(5)
O(3)–N(4)	1.288(5)
N(3)–N(4)	1.280(5)
Angles	
O(1)–Zn(1)–O(4)	116.07(14)
O(1)–Zn(1)–O(2)	78.16(13)
O(4)–Zn(1)–O(2)	102.8(2)
O(1)–Zn(1)–N(2)	143.7(2)
O(4)–Zn(1)–N(2)	100.10(14)
O(2)–Zn(1)–N(2)	91.16(14)
O(1)–Zn(1)–N(1)	98.05(13)
O(4)–Zn(1)–N(1)	99.92(14)
O(2)–Zn(1)–N(1)	156.2(2)
N(2)–Zn(1)–N(1)	77.98(13)
C(5)–N(1)–C(1)	118.7(4)
C(5)–N(1)–Zn(1)	115.1(3)
C(1)–N(1)–Zn(1)	126.0(3)
C(10)–N(2)–C(6)	119.3(4)
C(10)–N(2)–Zn(1)	125.0(3)
C(6)–N(2)–Zn(1)	115.6(3)

the two ends of the  $N_2O_3$  ligand provides the only significant violation of the 2-fold symmetry. Although a given molecule of the complex is chiral, the crystal as a whole is racemic. The chelate bite angles ( $L-M-L$ ) all have the expected values for the two bipy ligands,  $N(1)-Co(1)-N(2) = 76.8(3)^\circ$  and  $N(3)-Co(1)-N(4) = 76.9(3)^\circ$  and for  $N_2O_3$ ,  $O(1)-Co(1)-O(2) = 78.7(3)^\circ$ . The  $N_2O_3$  moiety appears to have its charge localized at O(1), since the distance  $N(5)-O(1)$ , 1.376(10) Å, is significantly longer than the two  $N-O$  distances at N(6):  $N(6)-O(2) = 1.292(10)$  Å and  $N(6)-O(3) = 1.286(10)$  Å. There is a lesser but still significant difference between the corresponding  $Co-O$  distances, with  $Co(1)-O(2)$  (2.061(7) Å) exhibiting the expected elongation as compared to that of  $Co(1)-O(1)$  (2.005(7) Å) as shown in Table 5.

The extended structure presents an extensive system of hydrogen bonding, in which the four crystallographically independent water molecules play a key role. The water structure is itself a significant structural entity in the present system. Three of the four water molecules donate hydrogen

**Table 4.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) and Their Estimated Standard Deviations for Complex **4**<sup>a</sup>

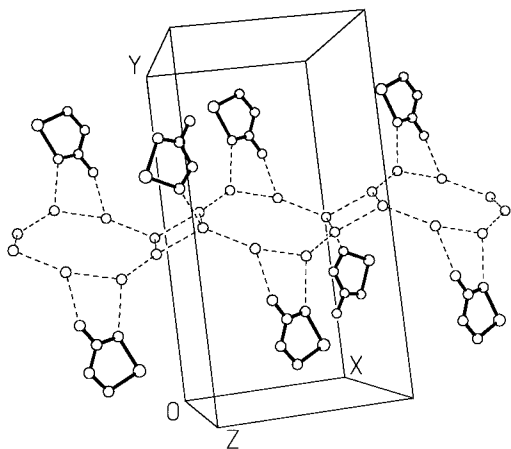
	x	y	z	$U_{eq}$
Co(1)	3149(2)	-1459(1)	3426(6)	29(1)
N(1)	4225(8)	-1461(5)	4798(6)	31(2)
N(2)	2393(9)	-448(4)	4092(5)	29(2)
C(1)	5241(11)	-1953(6)	5090(8)	39(3)
C(2)	6008(12)	-1912(6)	5932(8)	44(3)
C(3)	5751(11)	-1311(7)	6514(7)	44(3)
C(4)	4734(11)	-790(6)	6259(7)	40(3)
C(5)	3965(11)	-862(5)	5374(4)	32(3)
C(6)	2899(11)	-312(5)	4992(7)	31(2)
C(7)	2497(12)	313(6)	5529(8)	45(3)
C(8)	1505(11)	795(6)	5106(8)	40(3)
C(9)	951(11)	666(5)	4189(8)	35(3)
C(10)	1455(11)	33(5)	3706(8)	35(3)
N(3)	1671(9)	-1342(4)	2234(5)	28(2)
N(4)	1271(9)	-2067(4)	3889(5)	30(2)
C(11)	2009(12)	-958(6)	1429(7)	37(3)
C(12)	949(12)	-839(6)	709(8)	44(3)
C(13)	-442(12)	-1138(6)	838(7)	40(3)
C(14)	-746(11)	-1531(6)	1659(7)	41(3)
C(15)	355(11)	-1657(5)	2334(7)	27(2)
C(16)	128(11)	-2108(5)	3248(7)	32(2)
C(17)	-1080(12)	-2547(5)	3380(7)	37(3)
C(18)	-1155(11)	-2943(5)	4221(7)	37(3)
C(19)	-88(13)	-2886(6)	4933(8)	43(3)
C(20)	1103(12)	-2433(5)	4739(7)	38(3)
O(1)	4910(8)	-1084(4)	2700(5)	42(2)
O(2)	4074(7)	-2444(4)	2958(5)	36(2)
O(3)	5983(8)	-2879(4)	2109(5)	50(2)
N(5)	5784(10)	-1642(5)	2327(7)	48(3)
N(6)	5245(10)	-2327(5)	2450(6)	43(2)
O(1W)	6123(8)	-29(4)	1437(5)	46(2)
O(2W)	1390(8)	-4486(4)	4528(5)	56(2)
O(3W)	6344(10)	-4291(4)	2951(6)	72(3)
O(4W)	3512(9)	-3923(4)	3393(5)	56(2)

<sup>a</sup> The equivalent isotropic displacement parameter,  $U_{eq}$ , is calculated as  $U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^*$ .

**Table 5.** Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Complex **4**

Distances			
Co(1)–O(1)	2.005(7)	N(2)–C(6)	1.336(11)
Co(1)–O(2)	2.061(7)	N(3)–C(15)	1.332(11)
Co(1)–N(1)	2.113(7)	N(3)–C(11)	1.337(12)
Co(1)–N(3)	2.119(7)	N(4)–C(20)	1.345(11)
Co(1)–N(4)	2.127(8)	N(4)–C(16)	1.359(12)
Co(1)–N(2)	2.143(8)	O(1)–N(5)	1.376(10)
N(1)–C(1)	1.337(11)	O(2)–N(6)	1.292(10)
N(1)–C(5)	1.355(11)	O(3)–N(6)	1.286(10)
N(2)–C(10)	1.321(11)	N(5)–N(6)	1.333(11)
Angles			
O(1)–Co(1)–O(2)	78.7(3)	C(5)–N(1)–Co(1)	115.8(6)
O(1)–Co(1)–N(1)	94.3(3)	C(10)–N(2)–C(6)	118.0(9)
O(2)–Co(1)–N(1)	95.0(3)	C(10)–N(2)–Co(1)	126.1(7)
O(1)–Co(1)–N(3)	95.2(3)	C(6)–N(2)–Co(1)	115.9(7)
O(2)–Co(1)–N(3)	95.9(3)	C(15)–N(3)–C(11)	120.9(9)
N(1)–Co(1)–N(3)	166.8(3)	C(15)–N(3)–Co(1)	116.5(6)
O(1)–Co(1)–N(4)	164.7(3)	C(11)–N(3)–Co(1)	122.6(7)
O(2)–Co(1)–N(4)	89.0(3)	C(20)–N(4)–C(16)	116.3(9)
N(1)–Co(1)–N(4)	95.9(3)	C(20)–N(4)–Co(1)	127.1(7)
N(3)–Co(1)–N(4)	76.9(3)	C(16)–N(4)–Co(1)	116.6(6)
O(1)–Co(1)–N(2)	100.8(3)	N(5)–O(1)–Co(1)	113.9(5)
O(2)–Co(1)–N(2)	171.8(3)	N(6)–O(2)–Co(1)	111.5(6)
N(1)–Co(1)–N(2)	76.8(3)	N(6)–N(5)–O(1)	114.1(8)
N(3)–Co(1)–N(2)	92.3(3)	O(3)–N(6)–O(2)	120.2(9)
N(4)–Co(1)–N(2)	92.7(3)	O(3)–N(6)–N(5)	118.0(9)
C(1)–N(1)–C(5)	118.1(9)	O(2)–N(6)–N(5)	121.6(9)
C(1)–N(1)–Co(1)	125.7(7)		

bonds to the three independent oxygen atoms of the ligated  $N_2O_3$ , but more importantly, the water molecules form an eight-membered ring located about a crystallographic inversion center. As seen in Figure 3, this ring forms a hub about which the four



**Figure 3.** View of part of the infinite chain of water rings in the crystal structure of complex **4**. The principal, eight-membered water rings are centered at  $(-1/2, 1/2, 1/2)$ ,  $(1/2, 1/2, 1/2)$ , and so on, while the four-membered water rings are located at inversion centers at  $(0, 1/2, 1/2)$ ,  $(1, 1/2, 1/2)$ , and so on. Only the  $\text{CoN}_2\text{O}_3$  chelate ring is shown for the cobalt-containing complex.

**Table 6.** Bond Distances and Corresponding IR Stretching Frequencies for the Ionic and Coordinated Trioxodinitrate Anion

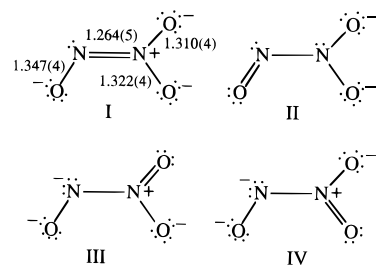
bond distance or IR data	compound		
	$\text{Na}_2\text{N}_2\text{O}_3$	<b>2</b>	<b>4</b>
$\text{N}=\text{N}$ (Å)	1.264(5)	1.280(5)	1.333(11)
$\nu_{\text{N-N}}$ ( $\text{cm}^{-1}$ )	1110, 1098	1071	1055, 1044
$\text{N}-\text{O}$ (Å)	1.347(4)	1.355(5)	1.376(10)
$\nu_{\text{N-O}}$ ( $\text{cm}^{-1}$ )	976	961	922

symmetry-related Co-containing complexes of one unit cell are distributed. The  $\text{N}_2\text{O}_3$  ligands form bridges between neighboring  $(\text{H}_2\text{O})_8$  rings in the extended structure, in addition to their role as chelating ligands within the cobalt complex. The hydrogen atoms of the water molecules were not located in the structure determination, and there is no way to assign donor and acceptor hydrogen atoms on the basis of the topology of the system. There is, furthermore, a possibility of disorder of the hydrogen atoms around the  $(\text{H}_2\text{O})_8$  ring. The ring of waters has a square-ended chair conformation. One edge of the water ring is joined by hydrogen bonds to the analogous edge of a neighboring eight-membered water ring, so that in fact the water structure forms an infinite chain propagated parallel to the crystallographic  $x$ -direction. The junction of two eight-membered water cycles is itself a four-membered ring which sits across a crystallographic inversion center. So, for example, with the choice of origin and coordinates that we have used, we have a four-membered water ring centered on  $(0.0, 0.5, 0.5)$  fused with an eight-membered ring centered at  $(0.5, 0.5, 0.5)$ , which in turn is fused to a four-membered ring that sits astride an inversion center at  $(1.0, 0.5, 0.5)$ , and so on.

We do not know whether the presence of such a high degree of water structure, with its necessary pejorative effect on overall structural rigidity, is implicated in the sharp drop-off of scattered X-ray intensity with increasing  $2\theta$  that we observed for this system.

### Concluding Remarks

Upon coordination some bond lengths of the trioxodinitrate anion seem to change in a systematic fashion as shown by the structural data and a careful analysis of the associated IR stretching absorptions. Table 6 summarizes the data. Although there are not many relevant structurally characterized compounds with  $\text{N}=\text{N}$  double bonds to compare (the  $\text{N}=\text{N}$  bond length is 1.23 Å in  $\text{HN}=\text{NH}$  and  $\text{FN}=\text{NF}$ , 1.24 Å in  $\text{MeN}=\text{NMe}$ , and 1.25 Å in coordinated *cis*- $\text{N}_2\text{O}_2^{2-}$ ),<sup>21,22</sup> it seems clear from the data that there is a significant weakening of the N to N bond



**Figure 4.** Resonance forms of the trioxodinitrate anion. The first resonance form indicates relevant distances (Å) in the uncoordinated anion.

upon coordination that is clearly reflected in the change of the  $\text{N}-\text{N}$  stretching frequencies that reach a negative shift of over  $50 \text{ cm}^{-1}$  for the Co complex. The bond remains closer to a double bond (for example, the  $\text{N}-\text{N}$  single bond in hydrazine is  $1.45 \text{ Å}$ <sup>23</sup> and the unusually long  $\text{N}-\text{N}$  bond distance in the neutral species  $\text{N}_2\text{O}_3$ , determined from a careful analysis of its microwave spectrum,<sup>23,24</sup> is  $1.86 \text{ Å}$ ). A similar lengthening of the nitrogen to lone-oxygen atom bond of the anion shows a comparable frequency shift in the IR spectrum. This oxygen atom is the most strongly bound to the metal atoms, and its more negative charge is consistent with its protonation in  $\text{HN}_2\text{O}_3^-$ . Of the four resonance forms of trioxodinitrate shown in Figure 4, form I has been proposed to be the most important for the free anion structure with minor contributions from forms II, III, and IV.<sup>2</sup> It seems that, for the coordinated anion, I, III, and IV are the only significant contributors.

There are a number of reports dealing with the decomposition and protonation reactions of trioxodinitrate,<sup>4,6,25,26</sup> and it would seem plausible that a similar weakening of the  $\text{N}-\text{N}$  bond occurs in the O- or N-monoprotonated forms as an initial step in the breaking of this bond. Most studies of the thermal instability of the anion were conducted in solutions without transition metal cations, and we were concerned at the outset that trioxodinitrate might form a Co-nitrosyl species or decompose to  $\text{NO}_2^-$  and  $\text{N}_2\text{O}$ . The fact that, under the conditions studied, disproportionation did not occur and stable trioxodinitrate complexes formed encourages further study of the coordination chemistry of the trioxodinitrate anion. We are presently pursuing this study.

**Acknowledgment.** Support from the Directorate General of Higher Education, Spain (Grant PB95-0792) is gratefully acknowledged. We thank Miss Isabel Pascual and Mr. Carlos E. Solano for assistance. We are thankful for support from the CONICIT, the Vicerrectoría de Investigación (Grant 115-96-339), and from the Escuela de Química, Universidad de Costa Rica.

**Supporting Information Available:** Complete listings of crystallographic data, hydrogen-bonding data and figure for complex **4**, bond lengths and angles, thermal parameters for complexes **2** and **4**, and description of models tested for a minor disorder component in the crystal structure of complex **2** (24 pages). Ordering information is given on any current masthead page.

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