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Nitrito–Nitro Linkage Isomerization in the Solid State. 1. X-ray Crystallographic Studies of *trans*-Bis(ethylenediamine)(isothiocyanato)nitrito- and *trans*-Bis(ethylenediamine)(isothiocyanato)nitrocobalt(III) Perchlorate and Iodide

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The nitrito–nitro isomerization in the solid state has been investigated by X-ray structure determinations of the perchlorate and iodide salts of *trans*-bis(ethylenediamine)(isothiocyanato)nitritocobalt(III), *trans*-$[Co(en)_2(NCS)(ONO)]X$, $X^- = ClO_4^-$ and I^-, and the corresponding nitro complexes. The intensity data refined by collected at 245 K (for the iodide compounds) or at 165 K or 163 K (for the perchlorate compounds) by use of a computer-controlled four-circle diffractometer. All compounds are monoclinic, space group $P2_1$ with $Z = 2$. The structures were refined by using full-matrix least-squares methods. In the final models, the scale factor, the positional parameters, and the anisotropic thermal parameters on all nonhydrogen atoms were refined to an R value based on F_o equal to 0.054 and 0.049, respectively, for the nitrito and nitro iodides and to 0.081 and 0.103, respectively, for the corresponding perchlorates. Each structure contains mononuclear cationic cobalt complexes and perchlorate or iodide counterions. The coordination around cobalt is close to O_h and, apart from the way of bonding of the ambidentate NO_2^- group, the structures are essentially identical. The structures of the two isomers indicate that the isomerization is intramolecular and that the reaction takes place in a plane by rotation of the NO_2^- group, most likely via a seven-coordinate transition state. The thermal isomerization of the perchlorate compound and the photochemical isomerization of the nitro perchlorate compound to the corresponding nitrito compound were both investigated by powder X-ray diffractometry. Both isomerizations proceed via the formation of a solid solution. The photochemically obtained nitrito compound gave a diffraction pattern identical with that of the original nitrito compound. Hence, the photochemical nitro → nitrito reaction also seems to take place by a rotation of the NO_2^- group.

Introduction

The study of kinetics and mechanism of substitution reactions and geometrical rearrangements in complexes has played an important part in the development of coordination chemistry from the days of Werner and Jørgensen up to the present time. Most investigations have been concerned with processes in solution, even though some reactions also may be studied in the solid state at moderate temperatures and pressures. Solid-state reactions of this type result in general in a breakdown of the long-range order in the crystal due to the differences in geometry between the initial and final states. However, the nitrito–nitro isomerization of the ambidentate NO_2^- ion in cobalt(III) complexes, discovered by Jørgensen[2] and later studied extensively by Adell and others,[3] is an example of a reaction which in some cases occurs with nearly complete retainment of crystallinity. Hence, the reaction may be studied by X-ray diffraction methods. From the structures one may infer whether the isomerization occurs by an intramolecular or by an intermolecular ligand transfer mechanism. It may also be possible to get some idea of the stereochemical course of the reaction.

In this article we will use the structures of the perchlorate and iodide salts of *trans*-bis(ethylenediamine)(isothiocyanato)nitritocobalt(III) and the corresponding nitro complexes for a brief discussion of the isomerization reactions involving the ambidentate NO_2^- ion. A more detailed discussion will be given in a following report[4] describing the isomerization of pentaamminenitritocobalt(III) dichloride.

The kinetics of the reactions have previously been studied by Adell,[3a,b] who found that the isomerization in the solid state follows a first-order rate law and that the reaction goes to virtual completion. We have collected the X-ray diffraction data for the unstable nitrito isomers at low temperature in order to freeze the isomerization reaction during the data collection. The structures of the corresponding nitro isomers were determined by using specimens obtained by room-temperature isomerization of single crystals of the corresponding nitrito complexes. The same single crystal of the perchlorate compounds was used for the two structure determinations. In this case the isomerization resulted in some disorder in the single crystal, the main effect of which was large anisotropic thermal parameters of some of the atoms (especially noticeable in the perchlorate group). To avoid this inconvenience the study of the iodide compounds was undertaken. The iodide ion has approximately the same size as the perchlorate ion.

Experimental Section

Preparation. Microcrystalline *trans*-$[Co(en)_2(NCS)(ONO)]ClO_4$ and *trans*-$[Co(en)_2(NCS)(ONO)]I$ were prepared as described by Adell.[3a] They were purified by repeated dissolution in cold water followed by precipitation with solid sodium perchlorate or potassium iodide until satisfactory elemental analyses were obtained.

Single crystals of the nitrito compounds suitable for X-ray investigation were obtained by slow evaporation of aqueous solutions at 278 K in order to reduce isomerization. Single crystals of the nitro compounds were obtained by a solid-state reaction, i.e., by aging the solid nitrito compounds at 293 K for at least 10 half-lives ($t_{1/2} = 320$ h and 220 h for the perchlorate and the iodide compounds, respectively[3a]). As the reaction proceeds, the color of the crystals changes from red to yellow.

Unit Cells and Space Groups. Survey oscillation and Weissenberg photographs gave $P2_1$ and $P2_1/m$ as possible space groups for all four compounds. Only $P2_1$ is compatible with the known geometry of the complex and the unit cell dimensions. The lattice constants and their estimated standard deviations were obtained by least-squares refinement of θ values determined according to ref 5 using Cu Kα radiation ($\lambda\alpha_1$ 1.540 562 Å). The temperature was the same as that used for collecting the complete three-dimensional diffraction data; see Table I. *trans*-$[Co(en)_2(NCS)(ONO)]I$, *trans*-$[Co(en)_2(NCS)(NO_2)]I$, *trans*-$[Co(en)_2(NCS)(ONO)]ClO_4$, and *trans*-$[Co(en)_2(NCS)(NO_2)]ClO_4$ are in the following denoted I, II, III, and IV, respectively. Cell parameters with estimated standard deviations are given in Table I.

Data Collection, Structure Determination, and Refinement. The three-dimensional intensity data were recorded with an Enraf-Nonius CAD-4 diffractometer equipped with a low-temperature attachment.[5] Cu radiation was used because of the fairly large amount of weak reflections and the fact that the crystals slowly deteriorate under X-ray radiation. Intensity data collection, data reduction, and structure refinements were performed as described previously.[6] Some details are given in Table II. Three standard reflections were used. They showed an approximately linear decrease in intensity with the time of exposure of the crystal. The overall decrease was approximately

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Table I. Crystal Data

	I	II	III	IV
compd	*trans*-$[Co(en)_2(NCS)(ONO)]I$	*trans*-$[Co(en)_2(NCS)(NO_2)]I$	*trans*-$[Co(en)_2(NCS)(ONO)]ClO_4$	*trans*-$[Co(en)_2(NCS)(NO_2)]ClO_4$
M_r	410.12	410.12	382.67	382.67
space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a, Å	9.3896 (4)[a]	9.288 (1)	9.265 (2)	9.371 (2)
b, Å	7.1609 (3)	7.220 (1)	7.2091 (8)	6.9224 (6)
c, Å	10.3759 (6)	10.509 (2)	10.847 (2)	11.025 (2)
β, deg	100.513 (5)	100.89 (1)	101.74 (1)	100.76 (2)
U, Å^3	685.9 (1)	692.1 (3)	709.4 (4)	702.6 (4)
Z	2	2	2	2
$F(000)$	400	400	392	392
D_m,[b] g cm^{-3}	1.9[c]	1.9[c]	1.8	1.8
D_c, g cm^{-3}	1.98	1.97	1.79	1.77
T, K	245	245	165	163
no. of reflections used for determination of cell dimensions	71	73	34	55

[a] Estimated standard deviations are given in parentheses throughout this paper. [b] Room temperature. [c] Density measurements were made on a mixture of two phases. The compounds of the second phase are monoclinic with $Z = 4$. $a = 12.951$ (5) Å, $b = 7.054$ (3) Å, $c = 15.456$ (6) Å, $\beta = 103.63$ (3)°, for the nitrito isomer and $a = 13.001$ (2) Å, $b = 7.014$ (1) Å, $c = 15.333$ (3) Å, $\beta = 101.54$ (1)° for the nitro isomer. The habit of the second phase is tabular c^*.

Table II. Data Collection and Least-Squares Refinement for Structures I-IV[a]

	I	II	III	IV
crystal habit	prismatic b^*	prismatic b^*	tabular c^*	tabular c^*
size, mm	0.195 × 0.095 × 0.040	0.170 × 0.100 × 0.078	0.162 × 0.117[b]	0.162 × 0.117[b]
takeoff angle, deg	3	3	5	5
no. of data sets	2	2	2	1
θ interval of data sets, deg	5-50; 50-70	5-50; 50-70	5-60; 60-70	5-70
$\Delta\omega$ interval (ω-2θ scan), deg	$0.75 + 0.50 \tan\theta$; $1.35 + 0.50 \tan\theta$	$1.40 + 0.50 \tan\theta$; $1.40 + 0.50 \tan\theta$	$1.00 + 0.50 \tan\theta$; $1.00 + 0.50 \tan\theta$	$1.00 + 0.50 \tan\theta$
μ(Cu Kα), cm^{-1}	296.0	293.4	134.4	135.7
range of transmission factors	0.086-0.397	0.063-0.258	0.200-0.368	0.200-0.367
T, K	245	245	165	163
no. of reflections with $I < 0$ given zero weight	32	57	31	49[c]
no. of reflections not measd due to collision	0	0	47	46
no. of independent reflections used in final refinement, m	1388	1364	1378	1253
no. of parameters refined, n	145	145	181	175[d]
R,[e] R_0,[f] R_w[g] for the assigned absolute confign	0.054, 0.056, 0.065	0.049, 0.055, 0.052	0.081, 0.084, 0.100	0.103, 0.127, 0.138
R, R_0, R_w for the opposite absolute confign	0.065, 0.068, 0.087	0.057, 0.063, 0.063	0.082, 0.085, 0.100	
$S = \{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)\}^{1/2}$	2.03	1.47	2.29	1.98
a (constant in weighting function)	0.0005	0.0005	0.001	0.003

[a] The data were recorded using graphite-monochromatized Cu Kα radiation (λ 1.541 838 Å). [b] Side (in an approximately equilateral triangle) and height. [c] 97 reflections with $0.5 \geq \lvert F_o\rvert/\lvert F_c\rvert \geq 2.0$ were also given zero weight. [d] The anisotropic temperature factor for N(4) could not be varied in the last cycles of refinement. [e] $R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. [f] $R_0 = R$ (including zero weight data). [g] $R_w = \{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2)/\Sigma w\lvert F_o\rvert^2\}^{1/2}$.

15% for all crystals studied. For the nitrito compounds, this decrease is probably not dependent on the isomerization reaction but on the changing crystal quality. The intensities of all reflections were corrected for this intensity change.

The positions of cobalt, sulfur, and iodine or chlorine were deduced from three-dimensional Patterson maps. The remaining nonhydrogen atoms were obtained from difference electron density maps. Most of the hydrogen atoms could also be located. However, no hydrogen atoms could be located in compound IV, probably due to a small deterioration of the crystal on isomerization. This crystal has also been exposed to X-radiation for a longer time than the others.

The hydrogen atoms were included in the final refinement of structures I-III with fixed positional and thermal parameters ($B = 5.0$ Å^2). The positional coordinates either were those obtained from the electron density maps or were calculated geometrically; see Table III. Tables III and IV give the refined parameters. The absolute configurations of structures I and II were determined by comparing the R_w values for the two enantiomers according to Hamilton.[7] The opposite absolute configurations were both rejected on the 0.005 level of significance. Structures III and IV were assigned the same configuration as II. I and II have opposite absolute configurations. However, we do not think that this is an effect of the isomerization; rather we attribute this to the fact that two different single crystals have been used in the data collection. Polar crystals of the type studied here consist of equal amounts of the two enantiomers.

The atomic scattering factors as well as the corrections for anomalous scattering of cobalt, iodine, chlorine, and sulfur were taken from ref 8. The extinction of the crystals was negligible.

The final difference electron density maps based on the parameters given in Tables III and IV were essentially featureless. The largest positive peak was about 1 e/Å^3 in all structures. The structures of the iodides had negative residuals in the vicinity of the iodine atom which were equal to 2.4 and 1.1 e/Å^3 in I and II, respectively. Tables of $\lvert F_o\rvert$ and $\lvert F_c\rvert$ are available.[9]

Description of the Structures

The general features of the structures are essentially the same, apart from the way of bonding of the NO_2^- group; see Figure 1. Each structure contains mononuclear complexes and X^- ions, $X^- = I^-$ or ClO_4^-. There are no or only very weak hydrogen bonds between the anions and the cations. Inter-

Table III. Positional Parameters for Structures I–IV

	I			II			III			IV		
atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Co	0.1901 (2)	$^{1}/_{4}$	0.2373 (1)	0.1868 (2)	$^{1}/_{4}$	0.2384 (1)	0.1956 (2)	$^{1}/_{4}$	0.2352 (1)	0.1948 (3)	$^{1}/_{4}$	0.2354 (2)
I	0.24559 (8)	0.2644 (3)	0.73998 (6)	0.24627 (8)	0.2381 (4)	0.74328 (6)						
Cl							0.2475 (4)	0.2366 (5)	0.7431 (3)	0.2495 (5)	0.2383 (9)	0.7491 (4)
S	0.3577 (3)	−0.2757 (5)	0.4848 (3)	0.3660 (3)	0.7763 (6)	0.4823 (2)	0.3586 (4)	0.7755 (5)	0.4807 (2)	0.3676 (5)	0.7797 (9)	0.4948 (4)
O(1)	0.1255 (10)	0.7411 (15)	0.0821 (8)	0.1714 (11)	−0.1099 (15)	0.1526 (9)	0.1233 (10)	−0.2249 (13)	0.0731 (7)	0.1944 (30)	−0.1157 (30)	0.1511 (20)
O(2)	0.1201 (8)	0.4522 (11)	0.1222 (7)	0.0304 (10)	0.0752 (16)	0.0300 (7)	0.1216 (9)	0.0606 (10)	0.1214 (6)	0.0499 (17)	0.0701 (25)	0.0331 (13)
O(3)							0.2663 (20)	0.1370 (22)	0.8575 (11)	0.2685 (31)	0.0966 (62)	0.8471 (22)
O(4)							0.0970 (12)	0.2438 (30)	0.6916 (16)	0.1168 (28)	0.2412 (38)	0.6888 (26)
O(5)							0.3273 (21)	0.3947 (36)	0.7562 (22)	0.2930 (50)	0.4058 (82)	0.7813 (69)
O(6)							0.3022 (20)	0.1245 (24)	0.6541 (12)	0.3245 (38)	0.1989 (76)	0.6760 (31)
N(1)	0.1660 (13)	0.6163 (15)	0.1634 (10)	0.1212 (9)	0.0462 (15)	0.1288 (8)	0.1747 (12)	−0.1031 (13)	0.1526 (9)	0.1422 (23)	0.0432 (27)	0.1255 (15)
N(2)	0.2576 (10)	0.0420 (13)	0.3456 (8)	0.2534 (9)	0.4574 (14)	0.3497 (7)	0.2590 (10)	0.4603 (16)	0.3413 (9)	0.2559 (13)	0.4614 (25)	0.3438 (13)
N(3)	0.1245 (11)	0.3740 (14)	0.3852 (9)	0.1238 (10)	0.1210 (13)	0.3823 (7)	0.1191 (12)	0.1278 (15)	0.3775 (9)	0.1077 (15)	0.1029 (22)	0.3675 (15)
N(4)	−0.0045 (9)	0.1449 (13)	0.1948 (8)	−0.0107 (8)	0.3566 (13)	0.2042 (7)	−0.0051 (11)	0.3608 (14)	0.1973 (9)	−0.0028 (11)	0.3571 (23)	0.2095 (12)
N(5)	0.2552 (10)	0.1287 (14)	0.0915 (9)	0.2484 (10)	0.3852 (16)	0.0961 (7)	0.2454 (14)	0.3923 (15)	0.0933 (10)	0.2356 (13)	0.4193 (22)	0.0993 (12)
N(6)	0.3805 (10)	0.3654 (15)	0.2750 (9)	0.3815 (9)	0.1376 (14)	0.2722 (8)	0.3801 (12)	0.1455 (16)	0.2769 (11)	0.3743 (18)	0.1552 (30)	0.2756 (16)
C(1)	0.3007 (10)	−0.0883 (15)	0.4045 (10)	0.3040 (10)	0.5926 (15)	0.4030 (8)	0.3034 (13)	0.5936 (16)	0.3970 (10)	0.3019 (15)	0.5950 (27)	0.4090 (13)
C(2)	−0.0231 (13)	0.3011 (15)	0.3982 (11)	−0.0229 (11)	0.1964 (14)	0.4005 (9)	−0.0231 (17)	0.2165 (22)	0.3812 (13)	−0.0196 (21)	0.2039 (27)	0.3793 (19)
C(3)	−0.1023 (11)	0.2569 (21)	0.2565 (11)	−0.1109 (9)	0.2437 (25)	0.2694 (8)	−0.1088 (14)	0.2527 (24)	0.2511 (14)	−0.1134 (14)	0.2336 (27)	0.2593 (16)
C(4)	0.4159 (14)	0.1520 (23)	0.1114 (12)	0.4089 (13)	0.3747 (28)	0.1157 (12)	0.4166 (15)	0.3726 (24)	0.1185 (18)	0.4182 (23)	0.3882 (48)	0.1178 (24)
C(5)	0.4558 (14)	0.3374 (23)	0.1623 (15)	0.4514 (13)	0.1863 (23)	0.1651 (17)	0.4569 (13)	0.1997 (22)	0.1751 (23)	0.4515 (16)	0.2240 (34)	0.1826 (32)
H(1N3)	0.092	0.478	0.366	0.075	−0.010	0.360	0.064	−0.021	0.338			
H(2N3)	0.188	0.375	0.503	0.188	0.122	0.462	0.159	0.241	0.454			
H(1N4)	−0.024	0.117	0.114	−0.009	0.307	0.121	−0.028	0.356	0.126			
H(2N4)	−0.002	0.019	0.236	0.017	0.466	0.230	0.035	0.526	0.218			
H(1N5)	0.207	0.174	0.022	0.204	0.342	0.014	0.217	0.352	0.012			
H(2N5)	0.218	0.015	0.081	0.230	0.496	0.102	0.213	0.528	0.063			
H(1N6)	0.370^a	0.494^a	0.290^a	0.330	−0.015	0.330	0.374	0.003	0.236			
H(2N6)	0.436^a	0.308^a	0.351^a	0.430	0.201	0.362	0.435	0.199	0.366			
H(1C2)	−0.098	0.425	0.407	−0.052	0.105	0.484	−0.120	0.178	0.412			
H(2C2)	−0.067	0.153	0.461	0.026	0.317	0.477	0.030	0.365	0.420			
H(1C3)	−0.133	0.371	0.236	−0.144	0.146	0.237	−0.160	0.112	0.205			
H(2C3)	−0.133	0.138	0.258	−0.211	0.266	0.262	−0.184	0.355	0.230			
H(1C4)	0.412	0.087	0.038	0.444	0.403	0.075	0.407	0.419	0.047			
H(2C4)	0.436	0.036	0.152	0.458	0.475	0.181	0.474	0.471	0.183			
H(1C5)	0.423	0.452	0.090	0.426	0.076	0.059	0.409	0.057	0.112			
H(2C5)	0.528	0.390	0.210	0.547	0.159	0.201	0.532	0.122	0.176			

[a] The parameter has been calculated geometrically.

Table IV. Anisotropic Thermal Parameters ($\beta_{ij} \times 10^4$) for Structures I-IV[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				I						II		
Co	74 (2)	29 (3)	35 (1)	1 (3)	−4 (1)	6 (2)	95 (2)	127 (3)	38 (1)	3 (3)	1 (1)	−6 (2)
I	164 (1)	96 (2)	71 (1)	13 (1)	21 (1)	9 (1)	196 (1)	166 (2)	93 (1)	12 (2)	30 (1)	0 (1)
S	124 (4)	54 (7)	66 (2)	0 (4)	−28 (2)	9 (3)	145 (3)	117 (7)	104 (2)	−9 (4)	−31 (2)	4 (3)
O(1)	244 (16)	66 (16)	117 (9)	−18 (20)	−8 (9)	7 (15)	202 (15)	200 (23)	179 (13)	−4 (16)	−3 (11)	−96 (15)
O(2)	94 (10)	43 (14)	56 (7)	2 (10)	0 (7)	26 (8)	201 (15)	365 (30)	65 (8)	−30 (17)	−10 (9)	−68 (12)
N(1)	165 (18)	68 (20)	78 (11)	9 (16)	−63 (11)	17 (13)	106 (12)	221 (24)	68 (8)	−38 (14)	42 (8)	−56 (11)
N(2)	101 (13)	42 (17)	54 (8)	21 (12)	−11 (8)	28 (10)	114 (12)	183 (21)	56 (7)	11 (13)	−4 (7)	−7 (10)
N(3)	113 (14)	54 (19)	57 (9)	−6 (13)	27 (9)	10 (11)	148 (13)	114 (18)	44 (6)	30 (13)	23 (7)	6 (9)
N(4)	94 (12)	59 (17)	49 (8)	10 (12)	−10 (8)	−19 (10)	83 (9)	165 (19)	66 (7)	−20 (11)	3 (6)	26 (10)
N(5)	89 (12)	70 (18)	71 (9)	19 (13)	5 (8)	−23 (11)	124 (12)	289 (26)	57 (7)	−71 (16)	20 (7)	11 (12)
N(6)	76 (12)	89 (20)	57 (9)	−16 (13)	1 (8)	1 (11)	87 (11)	173 (21)	86 (9)	−10 (12)	4 (8)	−24 (11)
C(1)	49 (12)	68 (22)	54 (10)	−23 (13)	−7 (9)	−11 (12)	82 (12)	156 (23)	47 (8)	28 (14)	−12 (7)	9 (12)
C(2)	96 (15)	110 (32)	68 (11)	−14 (14)	29 (10)	13 (12)	113 (13)	159 (29)	84 (10)	19 (13)	47 (9)	−5 (10)
C(3)	105 (14)	71 (19)	100 (11)	10 (22)	18 (10)	−7 (20)	92 (10)	199 (22)	85 (8)	5 (23)	29 (7)	49 (21)
C(4)	74 (16)	210 (34)	73 (14)	49 (20)	4 (11)	−6 (18)	91 (16)	402 (54)	118 (14)	−98 (25)	40 (12)	8 (21)
C(5)	74 (17)	199 (32)	90 (16)	−29 (19)	−7 (12)	3 (20)	66 (14)	302 (48)	208 (23)	−25 (17)	26 (14)	0 (24)
				III						IV		
Co	136 (2)	78 (3)	44 (1)	22 (2)	−10 (1)	−15 (2)	199 (4)	169 (6)	44 (1)	36 (4)	−15 (2)	−23 (3)
Cl	177 (4)	187 (7)	96 (3)	21 (5)	31 (3)	−7 (4)	163 (5)	388 (15)	111 (4)	123 (8)	14 (4)	10 (7)
S	218 (5)	127 (6)	75 (2)	−9 (5)	−27 (3)	−26 (4)	188 (6)	298 (13)	101 (3)	24 (7)	−44 (4)	−35 (6)
O(1)	250 (15)	78 (14)	84 (7)	8 (15)	5 (8)	−15 (11)	491 (50)	318 (49)	254 (32)	119 (40)	41 (30)	−147 (32)
O(2)	158 (12)	93 (13)	50 (6)	−7 (10)	15 (7)	−4 (7)	269 (26)	425 (46)	116 (15)	−79 (29)	8 (16)	−162 (23)
O(3)	513 (39)	358 (34)	129 (13)	131 (32)	143 (20)	54 (19)	455 (57)	1503 (198)	212 (31)	424 (85)	110 (36)	387 (70)
O(4)	165 (17)	611 (56)	291 (24)	−57 (31)	9 (15)	229 (36)	539 (60)	490 (70)	371 (44)	−213 (63)	−333 (46)	171 (53)
O(5)	375 (40)	708 (83)	451 (48)	−345 (52)	68 (34)	−72 (48)	727 (121)	1117 (201)	1223 (210)	522 (116)	−637 (129)	−923 (183)
O(6)	479 (39)	532 (51)	129 (14)	43 (38)	122 (20)	−140 (24)	562 (72)	1547 (239)	395 (57)	−93 (126)	357 (60)	−79 (97)
N(1)	194 (17)	99 (16)	70 (8)	2 (13)	−13 (9)	−13 (9)	309 (33)	293 (43)	95 (15)	−79 (34)	95 (21)	−72 (20)
N(2)	134 (13)	198 (22)	81 (10)	30 (15)	−30 (9)	−86 (13)	97 (14)	401 (46)	116 (15)	107 (21)	−46 (11)	−119 (22)
N(3)	169 (15)	171 (21)	64 (9)	41 (15)	9 (9)	−9 (11)	125 (17)	265 (38)	154 (18)	−46 (20)	20 (14)	24 (21)
N(4)	143 (13)	148 (19)	85 (9)	−16 (14)	35 (9)	−20 (11)	72[b]	373[b]	122[b]	−36[b]	89[b]	−44[b]
N(5)	223 (19)	165 (21)	86 (10)	−60 (17)	79 (12)	−17 (11)	119 (15)	349 (40)	93 (11)	−128 (21)	53 (11)	−33 (18)
N(6)	105 (13)	170 (22)	132 (13)	−1 (15)	−25 (10)	−31 (14)	158 (20)	381 (47)	133 (18)	−75 (28)	−47 (16)	17 (24)
C(1)	155 (17)	158 (24)	51 (9)	22 (16)	−7 (10)	−18 (12)	95 (16)	342 (47)	75 (13)	12 (22)	−3 (12)	−4 (21)
C(2)	187 (21)	294 (44)	98 (13)	45 (22)	41 (13)	−32 (17)	188 (26)	327 (54)	125 (20)	126 (31)	−1 (18)	−38 (23)
C(3)	141 (16)	236 (29)	156 (16)	19 (27)	53 (13)	86 (24)	93 (15)	270 (46)	126 (16)	30 (23)	21 (12)	25 (22)
C(4)	106 (18)	296 (44)	217 (24)	−91 (24)	61 (17)	−33 (26)	141 (26)	658 (107)	195 (30)	−209 (46)	−13 (21)	94 (45)
C(5)	50 (14)	251 (41)	330 (37)	−25 (17)	−39 (18)	−30 (27)	48 (15)	373 (78)	385 (53)	−106 (29)	13 (23)	−62 (48)

[a] The temperature factor used is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + \ldots)]$. [b] Not varied in the last cycles of refinement.

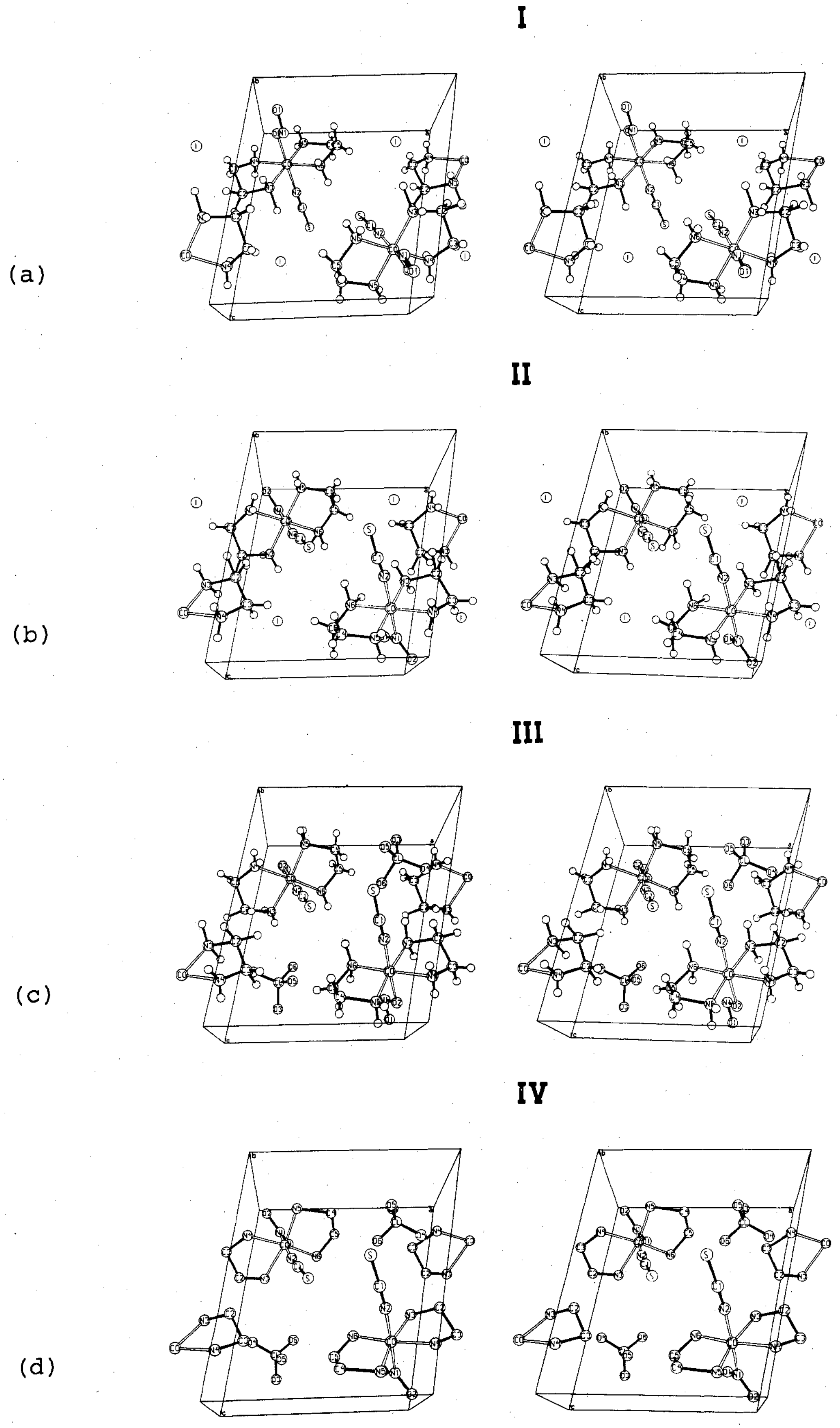

Figure 1. Stereoscopic pairs of drawings showing the packing of the cations and anions in the unit cells for (a) *trans*-[Co(en)$_2$(NCS)(ONO)]I (I), (b) *trans*-[Co(en)$_2$(NCS)(NO$_2$)]I (II), (c) *trans*-[Co(en)$_2$(NCS)(ONO)]ClO$_4$ (III), and (d) *trans*-[Co(en)$_2$(NCS)(NO$_2$)]ClO$_4$ (IV). I and II have different absolute configurations.

Table V. Bond Lengths (Å) and Bond and Torsion Angles (deg) in Structures I–IV

Bond Lengths

atoms	I	II	III	IV
Co–O(2)	1.915 (7)		1.875 (7)	
–N(1)		1.897 (10)		1.881 (18)
–N(2)	1.903 (9)	1.928 (9)	1.922 (11)	1.909 (16)
–N(3)	1.967 (9)	1.958 (8)	2.026 (10)	2.066 (16)
–N(4)	1.951 (9)	1.959 (8)	1.989 (10)	1.965 (11)
–N(5)	1.937 (9)	1.959 (9)	1.980 (11)	1.996 (14)
–N(6)	1.943 (10)	1.952 (9)	1.838 (11)	1.783 (17)
N(1)–O(1)	1.24 (1)	1.23 (2)	1.25 (1)	1.22 (3)
–O(2)	1.30 (1)	1.23 (1)	1.30 (1)	1.22 (2)
C(1)–N(2)	1.15 (1)	1.18 (1)	1.16 (2)	1.20 (2)
–S	1.62 (1)	1.61 (1)	1.62 (1)	1.64 (2)
N(3)–C(2)	1.51 (2)	1.51 (1)	1.47 (2)	1.41 (2)
N(4)–C(3)	1.45 (2)	1.50 (1)	1.45 (2)	1.52 (2)
N(5)–C(4)	1.50 (2)	1.47 (2)	1.56 (2)	1.70 (2)
N(6)–C(5)	1.49 (2)	1.44 (2)	1.48 (2)	1.44 (3)
C(2)–C(3)	1.55 (2)	1.50 (1)	1.50 (2)	1.46 (3)
C(4)–C(5)	1.45 (2)	1.48 (2)	1.41 (2)	1.35 (4)
Cl–O(3)			1.41 (1)	1.44 (3)
–O(4)			1.39 (1)	1.30 (3)
–O(5)			1.35 (2)	1.26 (6)
–O(6)			1.43 (2)	1.20 (4)

Bond Angles

atoms	I	II	III	IV
Co–O(2)–N(1)	115.1 (6)		115.0 (6)	
Co–N(1)–O(1)		121.5 (7)		119.6 (16)
O(1)–N(1)–O(2)	112.8 (10)	120.2 (11)	112.8 (9)	121.5 (20)
Co–N(2)–C(1)	175.8 (9)	170.1 (7)	173.8 (9)	176.0 (12)
N(2)–C(1)–S	178.3 (10)	176.3 (8)	176.3 (10)	178.2 (14)

Torsion Angles

atoms	I	II	III	IV
N(3)–C(2)–C(3)–N(4)	50 (1)	−49 (1)[a]	−55 (1)	−63 (2)
N(5)–C(4)–C(5)–N(6)	50 (1)	−49 (2)	−44 (2)	−32 (3)

[a] For definition of sign, see ref 22.

atomic bond distances and angles of interest for the following description are given in Table V.

The Cobalt(III) Complex Ions. There are no symmetry elements in the coordination polyhedra but the coordination geometry is close to O_h. The deviations can conveniently be described by using the range of the tilt and twist angles and the range of the edge lengths within the coordination polyhedron.[10] These quantities are given in Table VI. The systematic differences between the coordination polyhedra are small.

The Ligands. Bond distances and angles within the ethylenediamine and the NCS^- ligands are compatible with known structure data.[11,12] The conformation of the ethylenediamine ligands is $\delta\delta$[13] in I and, due to the different absolute configuration, $\lambda\lambda$ in II, III, and IV. Usually, the conformation in *trans*-bis(ethylenediamine) complexes is $\delta\lambda$,[14] as, for instance, in *trans*-$[Co(en)_2(NCS)(NO_2)]SCN$.[15] The torsion angles are given in Table V. The dimensions of the nitrite ion in $NaNO_2$ at 293 K are N–O = 1.240 (3) Å and O–N–O = 114.9 (5)°.[16] The angle has increased to about 120° in the nitro complexes. In the nitrito complexes the angle is close to 113° with unequal N–O bond distances. The distance N–O(coordinated to Co) is the longer of the two. The plane through the cobalt atom and the NO_2^- ligand divides the angle N(3)–Co–N(6) in two nonequal parts; see Table VII. If hydrogen bonds are formed, they are certainly weak. They have probably no importance either for the packing of anions and cations or for the isomerization. Possible hydrogen bonds are indicated in Table VIII.

The Perchlorate Ion. The oxygen atoms of the perchlorate ion have large thermal parameters especially in IV. The thermal motion is also pronouncedly anisotropic. These findings may indicate some degree of static or dynamic disorder within the group due to the absence of strong directional interactions, such as hydrogen bonding, between the perchlorate ion and its environment. The geometry of the ion is compatible with previous structural data.[11,12]

Geometry and Mechanism of the Isomerization Reaction $ONO^- \rightarrow NO_2^-$ in the Solid State

It is well-known that cobalt(III) forms more stable complexes with nitrogen donors than with oxygen donors;[17] hence nitro complexes have a larger thermodynamic stability than the corresponding nitrito complexes. The formation of cobalt(III) nitrito complexes is thus due to kinetic and not thermodynamic factors. Most of these complexes seem to be formed in weakly acidic solutions by the reaction of N_2O_3 and a cobalt(III) hydroxo ligand without rupture of the original cobalt–oxygen bond.[3e,f] The nitrito complex isomerizes both in solution and in the solid state to the corresponding nitro complex. The isomerization in solution is an intramolecular process.[3e,f] This study shows that this is also the case for the solid-state isomerization.

Figure 2 shows the reaction scheme. The O(1), O(2), and N(1) atoms are approximately situated in the same plane (also containing Co) before and after the rearrangement, indicating that the isomerization virtually takes place by rotation in this plane; cf. Table VII. The reaction proceeds by an intramolecular mechanism; otherwise, the nitrito nitrogen would have to move at least 4 Å. The rotation path is not restricted by steric hindrance, since no short van der Waals contact distances are obtained during the course of the reaction, assuming the ethylenediamine ligands to be rigid; see Figure 1. The final position of the NO_2^- ligand should be given by the energetically favored orientation. The rearrangement most likely proceeds via a seven-coordinate transition state, where the cobalt atom is bonded to both O(2) and N(1).

The isomerization of the perchlorate compound III has also been studied by powder diffractometry at 293 K; see Figure 3. A gradual shift of the powder pattern and consequently the cell dimensions occurs as the solid is changed from the nitrito to the nitro form. If two separate phases were present during the transformation, one should detect powder patterns from both phases. No such peaks were observed. Hence it is reasonable to assume that the transformation proceeds via the formation of a solid solution; i.e., the reaction is homogeneous.[18]

Irradiation of *trans*-$[Co(en)_2(NCS)(NO_2)]ClO_4$ (IV) gives a nitrito compound in ~80% yield.[19] We do not know whether this figure represents a maximum yield or the maximum

Table VI. Geometry of the Coordination Polyhedron in Structures I–IV

	I	II	III	IV	O_h symmetry
tilt angle,[a] deg	1.9	0.6	2.1	6.0	0.0
range of twist angles, deg	55.8–63.2	56.4–62.2	55.0–65.5	50.9–68.3	constant 60.0
range of edges, Å	2.66–2.84	2.66–2.86	2.66–2.85	2.56–2.89	constant
av of edges, Å	2.74	2.75	2.74	2.73	
displacement of Co atom from centroid of polyhedron, Å	0.02	0.01	0.10	0.10	0.0

[a] The tilt angle is the angle between the planes defined by the atoms O(2) or N(1), N(4), and N(5) and N(2), N(3), and N(6).

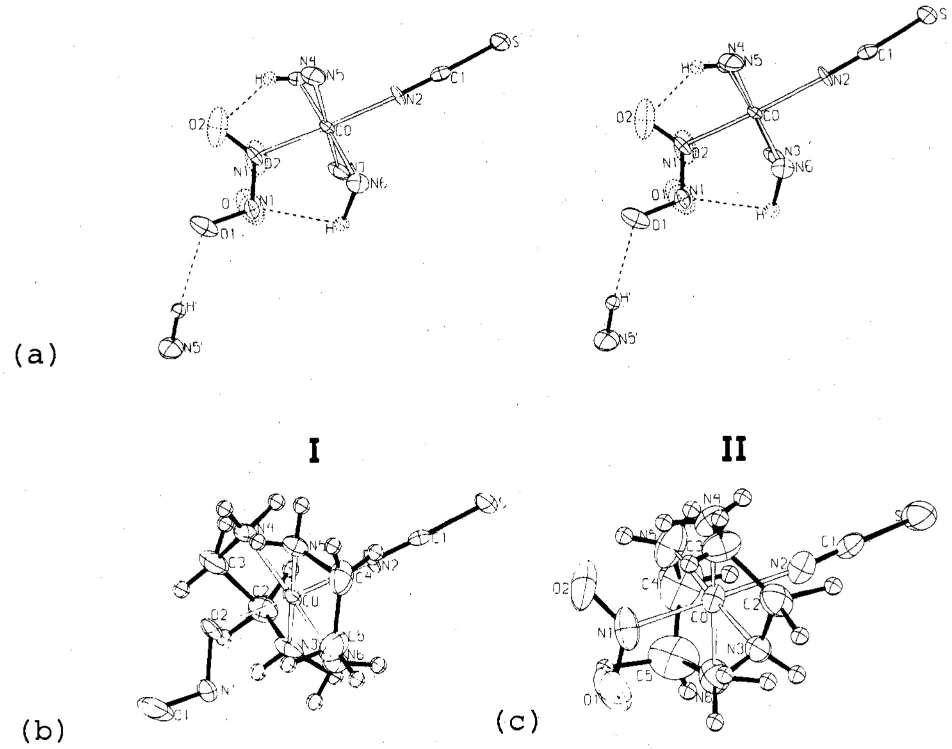

Figure 2. A possible pathway depicting the nitrito → nitro isomerization. In the stereoscopic figures (a) the full-drawn atoms with symbols to the right belong to structure I and the dashed with symbols to the left belong to structure II. The *y* parameters of these last atoms have been transformed to fit the absolute configuration of structure I. As a comparison, the entire complex in structures I (b) and II (c) are also shown. The ellipsoids for the nonhydrogen atoms represent 50% of the probability distribution.

Table VII. Angles between Selected Planes Showing the Orientation of the Nitrito/Nitro Ligand in Relation to the Ethylenediamine Ligands[a]

structure	planes	angle, deg	atoms	torsion angle, deg
I	1, 2	54.5	N(1)–O(2)–Co–N(3)	53.1 (8)
I	1, 3	39.0	N(1)–O(2)–Co–N(6)	−40.2 (8)
II	1, 3	35.9	O(1)–N(1)–Co–N(6)	34.1 (9)
III	1, 3	35.4	N(1)–O(2)–Co–N(6)	34.3 (8)
IV	1, 3	35.5	O(1)–N(1)–Co–N(6)	35.1 (20)

[a] The least-squares planes are fitted to the following atoms; plane 1, Co, O(1), O(2), N(1), N(2); plane 2, Co, O(2), N(2), N(3), N(5); plane 3, Co, O(2) or N(1), N(2), N(4), N(6). Torsion angles are included as a comparison.

Table VIII. Distances (A) and Angles (deg) Connected with Possible Hydrogen Bonding to the Nitrito/Nitro Ligand[a]

structure	X–H· · ·Y	X· · ·Y	H· · ·Y	X–H· · ·Y
I	$N(5^{i})$–$H(2N5^{i})\cdots O(1)$	3.02	2.14	173
II	N(6)–H(1N6)· · ·O(1)	2.77	2.25	96
II	N(4)–H(1N4)· · ·O(2)	2.81	1.99	142
III	$N(5^{ii})$–$H(2N5^{ii})\cdots O(1)$	2.97	1.98	156

[a] Superscripts refer to the following transformations of the coordinates *x*, *y*, *z*: (i) *x*, *y* + 1, *z*; (ii) *x*, *y* − 1, *z*.

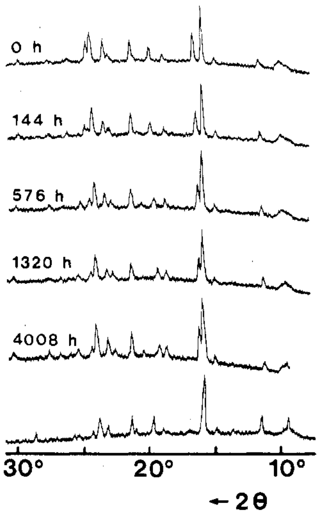

Figure 3. Powder diffractograms depicting the nitrito → nitro isomerization in the perchlorate compound as a function of time; $t_{1/2}$ = 320 h at 293 K. The last curve shows the powder pattern of the nitro compound prepared from an aqueous solution.

steady-state concentration that can be achieved under the experimental conditions used. The reaction proceeds by retainment of crystallinity, and the powder pattern of the illuminated sample indicates that the photochemical reaction produces a nitrito compound identical with that of III. The reaction presumably takes place by a rotation of the NO_2^- group in a way which is the reverse of that described above. Thus both the thermal nitrito–nitro isomerization and the reverse photochemical reaction proceed with a minimum of atomic and molecular movement. They could thus be classified as topochemical reactions.[20]

The structure of the nitro compound of the perchlorate formed by isomerization in the solid state is *not* identical with that prepared from an aqueous solution of the complex; see the last two diffractograms in Figure 3. The latter complex gives a monoclinic solid with the approximate unit cell dimensions *a* = 22.56 Å, *b* = 16.2 Å, *c* = 5.59 Å, and *β* = 135°.[21] There are probably no major differences between the cobalt complexes in these two nitro structures (since their IR spectra are identical), rather there is probably a difference in the packing of the ions. An example of a packing rearrangement following the isomerization will be given in a subsequent article describing the isomerization of $[Co(NH_3)_5ONO]Cl_2$.[4]

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Registry No. I, 69102-48-3; II, 69102-49-4; III, 36452-54-7; IV, 15638-75-2.

Supplementary Material Available: Listings of structure factor amplitudes for products I–IV (25 pages). Ordering information is given on any current masthead page.

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A Short Intramolecular Hydrogen Bond: Crystal Structure of a Tetradentate α-Amine Oxime Complex of Palladium(II)

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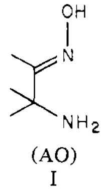
The crystal structure of [*N,N'*-(1,3-propanediyl)bis(2-amino-2-methyl-3-butanone oximato)]palladium(II) nitrate, $[Pd(PnAO\text{-}H)](NO_3)$, $[Pd(C_{13}H_{27}N_4O_2)]NO_3$, has been determined from three-dimensional X-ray diffraction counter data. Unit cell dimensions are $a = 11.0424$ (5), $b = 12.9114$ (5), and $c = 12.5871$ (7) Å. The density of 1.65 g/cm^3 calculated for four formula units per unit cell agrees with the flotation density of 1.66 g/cm^3. The space group is $P2_12_12_1$. A full-matrix least-squares refinement with 2838 independent reflections gave a final $R(F^2)$ value of 0.050. The structure consists of discrete, nearly square-planar palladium(II) complex cations and nitrate ions. A network of hydrogen bonding between amine nitrogens of the cation and oxygens of nitrate stabilizes the crystal structure. The steric requirements of the tetradentate PnAO are quite similar to two-coordinated bidentate AO ligands ($C_5H_{12}N_2O$), and a propylene bridge does not impose any significant constraint on the coordination geometry. Similarly, the size of the metal ion in going from palladium(II) to platinum(II) does not change the molecular parameters because of lanthanide contraction in the case of platinum(II). The average Pd–N(amine) and Pd–N(oxime) distances are 2.040 (4) and 1.969 (4) Å, respectively. These distances are quite similar to the comparable distances in related platinum(II) complexes. The short intramolecular O(1)···O(2) hydrogen bond (2.474 (5) Å) is apparently quite asymmetric and is equal to the corresponding bond in platinum(II) complexes, but significantly (0.05 Å) longer than that observed in the case of nickel(II) complexes. Other important average bond distances are N–O = 1.352 (5), C–N(oxime) = 1.278 (6), and C–N(amine) = 1.512 (6) Å.

Introduction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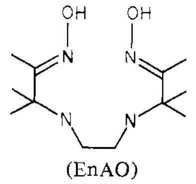
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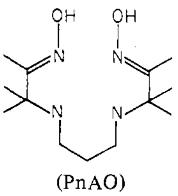
(PnAO)
III

Several metal complexes of α-amine oxime ligands (I–III) have been studied by X-ray and neutron diffraction to understand the effects of O···O distance and of crystallographic environment on the hydrogen atom position and the associated potential function. In these complexes it is possible to obtain a wide variation in O···O distance by changing the size of the metal ion and by varying the steric requirements of the ligand in the square plane about the metal from least constrained AO to the most constrained EnAO. The relatively small nickel(II) and cobalt(III) ions exhibit the shortest distances of 2.40–2.42 Å with the unconstrained AO ligand,[1-3] while the same ligand gives a longer (2.47 Å) distance with platinum(II).[4,5] Introduction of an ethylene bridge (EnAO) opposite the hydrogen bond increases the O···O distance from 2.42 Å in $[Ni(AO)_2\text{-}H]^{+2}$ to 2.47 Å in $[Ni(EnAO\text{-}H)]^+$.[6,7] A still longer distance (2.69 Å) is found with relatively larger copper(II) ions in the dimeric copper–EnAO complex.[8] A propylene bridge (PnAO) instead of an ethylene bridge does not impose too much constraint relative to AO, and only intermediate distances of 2.46 and 2.43 Å are found in square-pyramidal $[Cu(PnAO\text{-}H)ReO_4]$[9] and near-octahedral $[Co(PnAO\text{-}H)(NO_2)_2]$.[10] Thus, it is clear that a range of O···O distances from 2.40 to 2.70 Å could be obtained either by changing the steric requirements of the ligand or by changing the size of

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