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Structural Chemistry of the {CoNO}^{8} Group. Structure of *trans*-Perchloratonitrosylbis(ethylenediamine)cobalt Perchlorate, $[Co(NO)(C_2N_2H_8)_2(OClO_3)][ClO_4]$.[1]

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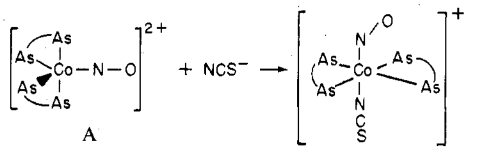
The crystal and molecular structure of $Co(NO)(en)_2(ClO_4)_2$ (en is ethylenediamine) has been determined by single-crystal x-ray diffraction. The compound crystallizes in space group C_{2h}^5-$P2_1/c$ with 4 molecules in a cell of dimensions a = 7.831 (3) Å, b = 15.996 (6) Å, c = 12.429 (4) Å, and cos β = −0.3949 (3). The observed and calculated densities are 1.91 and 1.89 g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure using the 1437 data with $F_o^2 \geq 3\sigma(F_o^2)$ gave R_1 = 3.2%. The structure consists of *trans*-$[Co(NO)(en)_2(OClO_3)]^+$ cations and perchlorate anions. The Co–NO distance is 1.806 (6) Å. The CoNO group is strongly bent and the oxygen atom is disordered between two positions above the en rings. The refined Co–N–O angles are 135 (1) and 141 (2)°. An alternative description of the disorder with N–O distances fixed at 1.15 Å gave Co–N–O angles of 122 and 123°. The Co–O distance of the coordinated perchlorate ion is 2.360 (4) Å. Both perchlorate ions in the structure are ordered and involved in an extensive hydrogen-bonding network.

Introduction

In recent years there has been considerable interest in the structural, chemical, and electronic properties of complexes of the {CoNO}^{8} group.[2] This interest stems in part from the ability of this group to form five-coordinate complexes with a range of Co–N–O angles and coordination geometries as well as six-coordinate complexes with a strongly bent Co–N–O moiety.[3] In spite of the demonstrated existence of two different coordination numbers for {CoNO}^{8} complexes there is to our knowledge only one well-characterized example[5] of the conversion of a five-coordinate complex containing the {CoNO}^{8} group into a six-coordinate complex by the addition of a unidentate ligand. We have previously demonstrated that reaction 1 results in the conversion of the trigonal-bipyramidal five-coordinate $[Co(NO)(das)_2]^{2+}$ cation[6] A which has a linearly coordinated NO group in the equatorial position into the six-coordinate complex B with a strongly bent CoNO group. The transformation of A into B results in a large decrease in the NO stretching frequency and in the N 1s binding energy as shown. The chemical reactivities of the coordinated NO group of A and B differ dramatically.



(1)

A

ν_{NO} 1852 cm^{-1}
Co–N–O = 178°
$E_B(N_{1s})$ = 402.3 eV

B

ν_{NO} 1567 cm^{-1}
Co–N–O = 132°
$E_B(N_{1s})$ = 399.1 eV

In order to better understand the scope of reaction 1 and to further explore the behavior of the {CoNO}^{8} group other examples of five- and six-coordinate {CoNO}^{8} complexes related by a simple ligand addition reaction have been sought. Another potential pair of five- and six-coordinate {CoNO}^{8} complexes[7] are $Co(NO)(en)_2(ClO_4)_2$ (C) and $[Co(NO)(en)_2Cl][ClO_4]$ (D). A structure determination of D[8] has already shown it to contain the six-coordinate $[Co(NO)(en)_2Cl]^+$ cation with Co–N–O = 124°. From the similarity of the NO stretching frequencies of C and D (1668 and 1611 cm^{-1}, respectively), it seemed likely that their {CoNO}^{8} groups were similar. On the other hand, the difference in their colors suggested that their overall structures might differ significantly. In view of the weak coordinating ability of the ClO_4^- ion it seemed plausible that C might possess five-coordinate tetragonal-pyramidal coordination geometry with a strongly bent CoNO group. The stereochemistry of C is of further interest because it is an intermediate in a convenient synthesis[9] of

Co(NO)(dtc)$_2$ and of numerous other six-coordinate analogues of D.[7] The x-ray structure determination of C is described below.

Experimental Section

Small, black, well-formed crystals of Co(NO)(en)$_2$(ClO$_4$)$_2$ were grown by slowly cooling an oxygen-free methanol solution of the complex under nitrogen. Preliminary x-ray photographs (Mo Kα) showed monoclinic symmetry and the following systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. These conditions are unique for space group C_{2h}^5-$P2_1/c$. Cell constants (at 23 ± 2 °C) were determined on a Picker FACS-I diffractometer from a least-squares refinement of the setting angles for 17 reflections with $25° < 2\theta < 35°$ which had been centered automatically using Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å). The cell constants are a = 7.831 (3) Å, b = 15.996 (6) Å, c = 12.429 (4) Å, and cos β = −0.3949 (3). The observed density of 1.91 g cm^{-3}, determined by flotation in CH$_2$Br$_2$–C$_6$H$_5$Br, agrees with the calculated density of 1.89 g cm^{-3} for four molecules per cell.

A total of 1895 data with $2\theta \leq 40°$ were collected using graphite-monochromated Mo Kα radiation and θ–2θ scans. The θ–2θ axis of the monochromator was perpendicular to the θ–2θ axis of the diffractometer. The takeoff angle was 1.7° and the θ–2θ scan had a base width of 1.4°, with a dispersion factor being applied at higher 2θ values. The scan rate was 1°/min with 10-s backgrounds measured at the two extremes of the scan. Three standard reflections were monitored after every 100 measurements. There was no evidence for crystal decomposition during the period of data collection. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[10] The value for p in the standard expression[10] for $\sigma(F^2)$ was taken as 0.05.

The linear absorption coefficient for Mo Kα radiation is 16.9 cm^{-1} and an absorption correction was carried out.[11] The data crystal had approximate dimensions 0.25 × 0.25 × 0.10 mm, and the magnitude of the absorption correction ranged from 0.75 to 0.84.

The structure was solved using the MULTAN package[12] and the 254 reflections with $|E| \geq 1.50$ were used to generate an E map. The positions of the Co atom and the two perchlorate groups were found on this map. This partial structure was used to obtain the complete structure by a series of structure factor calculations, least-squares refinements, and difference electron density maps.

Refinement of the structure was based on F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized, where $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors for Co were from Cromer and Waber[13] while the factors for Cl, O, N, and C were from ref 14. The effects of anomalous dispersion were included for Co and Cl by using the values of Cromer.[15] The scattering factors for hydrogen were obtained from Stewart, Davidson, and Simpson.[16]

Refinement of the structure proceeded smoothly to $R_1 = \sum|F_o - F_c|/\sum|F_o|$ = 6.0%, for the 1437 data with $F_o^2 \geq 3\sigma(F_o^2)$. At this stage, the hydrogen atoms were found on a difference map and included in the structure factor calculations as fixed contributors. Subsequent anisotropic refinement of all nonhydrogen atoms reduced R_1 to 4.5%. The largest peak on a difference map after this refinement (0.93 e Å^{-3}) was in a position consistent with a disordered oxygen of the NO group. Additional anisotropic refinement with each oxygen position assigned an occupancy factor of 0.5 yielded R_1 = 0.032 and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ = 0.044 for 199 variables. A final difference map after this refinement showed no significant residual electron density in the region of the NO group. The maximum residual density (0.43 e Å^{-3}) occurred in the region of the coordinated perchlorate anion. The standard deviation of an observation of unit weight was 1.39. The value of R_1 for all 1895 data was 0.048 and R_2 was 0.049

The abnormally short N–O distances (≤1 Å) and the shape of the thermal ellipsoid for N(5) suggested unresolved disorder of the N atom of the nitrosyl group. Such disorder was included in an alternative model by using group refinement techniques.[17] The N and O positions from the previous anisotropic model were used to define initial coordinates for two NO groups with fixed N–O distances of 1.15 Å. In subsequent refinements 13 group parameters were varied: three positional and two rotational coordinates for each linear group; a relative occupancy factor; one isotropic thermal parameter for the N atoms; and one isotropic thermal parameter for the O atoms. All other atoms in the structure were refined anisotropically. This model (185 total variables) converged to R_1 = 0.035 and R_2 = 0.050 for the 1437 data with $F_o^2 > 3\sigma(F_o^2)$. The parameters for the other atoms in the structure did not differ significantly from those of the previous model with a single anisotropic N atom and disordered anisotropic O atoms. For comparison, an earlier refinement having a single *isotropic* N atom and disordered *isotropic* O atoms converged to R_1 = 0.035 and R_2 = 0.049 for 184 variables.

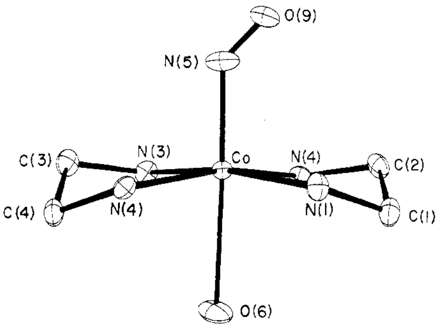


Figure 1. Perspective view of the [Co(NO)(en)$_2$(OClO$_3$)]$^+$ cation. For clarity hydrogen atoms have been omitted and only O(6) of the coordinated ClO$_4^-$ ion is shown. O(9) is one of the positions of the disordered oxygen atom of the nitrosyl group.

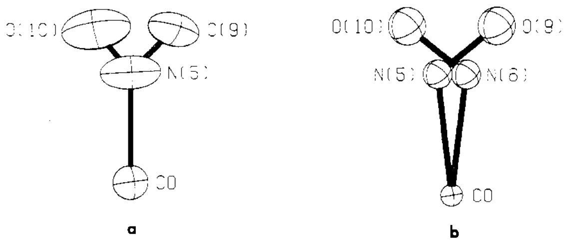


Figure 2. (a) Geometry of the CoNO fragment after refinement of a single anisotropic N atom and two disordered anisotropic O atoms. See Tables II and III for bond distances and angles associated with this model. Ellipsoids enclose 50% of the probability distribution. (b) Geometry of the CoNO moiety after refinement as two disordered NO groups with N–O = 1.15 Å. Co–N(5) = 1.805 (13), Co–N(6) = 1.803 (17) Å; Co–N(5)–O(9) = 122.7 (8), Co–N(6)–O(10) = 122.0 (11)°. Ellipsoids enclose 16% of the probability distribution.

A list of structure factors for the model with a single anisotropic N atom in the nitrosyl group and disordered ansiotropic O atoms is available as supplementary material. The final structural parameters for this model are in Table I. Selected interatomic distances are in Table II and selected interatomic angles are in Table III. The rms amplitudes of vibration along principal axes are in Table IV. The group parameters for the alternative description of the disordered NO ligand and the derived fractional coordinates for the atoms appear in Tables V and VI.

Results and Discussion

The determination of the structure of C shows that the compound is six-coordinate in the solid state and is properly formulated as *trans*-[Co(NO)(en)$_2$(OClO$_3$)][ClO$_4$]. A perspective view of the cation of C is shown in Figure 1.

A primary feature of interest in C is the geometry of the {CoNO}^{8} group. Figure 1 shows that the group has the expected strongly bent geometry which has been found in other six-coordinate complexes.[3,5,8,18] The NO group is disordered and two well-resolved positions for the O atom are refined satisfactorily. These two O atom positions can be combined with a single anisotropically vibrating N atom to give the disorder model for the CoNO fragment shown in Figure 2a. Although the model is mathematically well behaved, the N–O distances of 1.005 (9) and 0.911 (10) Å are unrealistically short. Correction for thermal motion assuming a riding model increases the distances somewhat to 1.044 (11) and 0.987 (15) Å, respectively, but these corrected distances are still shorter than those normally found for ordered metal nitrosyl complexes.[18] Moreover, the thermal ellipsoid of the N atom is elongated normal to the Co–N bond. Such behavior of

Table I. Atomic Positional and Thermal Parameters for $Co(NO)(C_4N_4H_{16})(ClO_4)_2$

Atom	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Co	−0.038 81 (8)	0.122 93 (3)	0.243 09 (5)	129.5 (14)	21.42 (27)	45.6 (6)	−6.1 (5)	32.2 (6)	−4.14 (28)
Cl(1)	0.352 78 (17)	0.370 83 (6)	0.219 41 (10)	194.3 (29)	27.2 (5)	64.9 (11)	−2.7 (9)	62.7 (14)	−2.4 (6)
Cl(2)	0.077 82 (15)	0.134 45 (6)	−0.009 73 (9)	153.6 (25)	27.9 (5)	43.0 (9)	−8.7 (9)	37.8 (12)	−2.3 (5)
O(1)	0.433 2 (6)	0.295 12 (22)	0.277 0 (4)	380 (13)	36.7 (18)	108 (4)	18 (4)	56 (6)	14.7 (22)
O(2)	0.428 7 (6)	0.440 67 (23)	0.295 5 (4)	312 (11)	40.0 (17)	129 (5)	−17 (4)	82 (6)	−30.2 (23)
O(3)	0.387 2 (6)	0.379 82 (23)	0.116 6 (3)	315 (11)	70.1 (24)	79 (4)	−14 (4)	98 (5)	2.0 (23)
O(4)	0.155 7 (5)	0.367 34 (22)	0.188 2 (4)	208 (10)	52.9 (21)	163 (6)	−15 (3)	109 (6)	−12.0 (25)
O(5)	0.140 0 (7)	0.205 54 (28)	−0.046 1 (4)	406 (15)	71.3 (27)	169 (6)	−56 (5)	22 (8)	69 (3)
O(6)	0.096 2 (6)	0.147 2 (3)	0.106 5 (3)	231 (10)	145 (4)	49 (3)	−38 (5)	60 (5)	−14.4 (28)
O(7)	−0.112 3 (5)	0.118 73 (26)	−0.083 9 (3)	169 (9)	90.7 (28)	81 (4)	−16 (4)	24 (5)	−31.4 (24)
O(8)	0.191 4 (6)	0.067 34 (28)	−0.011 5 (5)	299 (13)	57.0 (24)	238 (8)	30 (4)	45 (8)	−62 (3)
N(1)	−0.276 3 (5)	0.093 99 (24)	0.114 6 (3)	137 (9)	34.7 (17)	69 (4)	−22 (3)	43 (5)	−9.2 (21)
N(2)	−0.123 5 (5)	0.240 04 (22)	0.206 9 (3)	157 (9)	27.3 (16)	66 (4)	6 (3)	22 (5)	−6.3 (19)
N(3)	0.218 6 (5)	0.152 30 (23)	0.348 4 (3)	154 (9)	28.8 (16)	40 (3)	−2.7 (29)	20 (4)	−1.2 (18)
N(4)	0.055 6 (6)	0.008 18 (21)	0.258 1 (4)	223 (10)	20.1 (15)	79 (4)	−4 (3)	46 (5)	−7.4 (20)
N(5)	−0.122 5 (10)	0.111 6 (4)	0.358 5 (5)	326 (17)	64 (3)	82 (6)	−32 (6)	112 (8)	−6 (3)
C(1)	−0.402 2 (7)	0.167 4 (3)	0.087 1 (4)	105 (10)	52.4 (27)	74 (5)	2 (4)	18 (6)	−8.6 (29)
C(2)	−0.286 6 (7)	0.242 5 (3)	0.093 6 (5)	200 (13)	37.2 (24)	75 (5)	28 (5)	28 (7)	6.2 (27)
C(3)	0.343 1 (7)	0.079 7 (3)	0.354 8 (4)	138 (11)	46.2 (25)	61 (4)	26 (4)	15 (6)	−3.5 (27)
C(4)	0.237 4 (7)	0.002 2 (3)	0.358 3 (5)	224 (14)	32.5 (23)	87 (5)	31 (4)	44 (7)	1.6 (27)
O(9)[a]	−0.231 7 (14)	0.133 5 (6)	0.373 1 (10)	316 (26)	93 (7)	116 (10)	55 (10)	149 (15)	26 (6)
O(10)[a]	−0.106 3 (21)	0.079 1 (8)	0.422 0 (11)	547 (47)	113 (9)	146 (14)	9 (16)	208 (22)	37 (9)

Atom	x	y	z	Atom	x	y	z
H(1)[b]	−0.340	0.060	0.125	H(9)	−0.467	0.172	0.150
H(2)	−0.258	0.072	0.038	H(10)	−0.513	0.161	−0.002
H(3)	−0.031	0.263	0.208	H(11)	−0.242	0.242	0.043
H(4)	−0.137	0.262	0.268	H(12)	−0.353	0.300	0.085
H(5)	0.220	0.160	0.425	H(13)	0.380	0.080	0.275
H(6)	0.263	0.201	0.321	H(14)	0.459	0.087	0.426
H(7)	0.068	0.000	0.179	H(15)	0.180	0.000	0.425
H(8)	−0.014	−0.032	0.250	H(16)	0.314	−0.055	0.355

[a] O(9) and O(10) are the two positions for the oxygen of the disordered NO group. [b] The hydrogen atoms were treated as fixed contributors with their isotropic temperature factors, B, set equal to 5.0 Å^2.

Table II. Selected Bond Distances (Å)

Co-N(1)	1.969 (4)	C(4)-N(4)	1.479 (6)
Co-N(2)	1.979 (4)	N(5)-O(9)	1.005 (9) (1.044 (11))[a]
Co-N(3)	1.978 (4)	N(5)-O(10)	0.911 (10) (0.987 (15))[a]
Co-N(4)	1.960 (4)	Cl(1)-O(1)	1.421 (4)
Co-N(5)	1.806 (6)	Cl(1)-O(2)	1.433 (4)
Co-O(6)	2.360 (4)	Cl(1)-O(3)	1.414 (4)
N(1)-C(1)	1.484 (6)	Cl(1)-O(4)	1.436 (4)
C(1)-C(2)	1.487 (7)	Cl(2)-O(5)	1.382 (4)
C(2)-N(2)	1.482 (6)	Cl(2)-O(6)	1.409 (4)
N(3)-C(3)	1.498 (6)	Cl(2)-O(7)	1.430 (4)
C(3)-C(4)	1.501 (7)	Cl(2)-O(8)	1.400 (4)

[a] Corrected for riding motion.

Table III. Selected Bond Angles (deg)

N(5)-Co-N(4)	94.11 (28)	O(1)-Cl(1)-O(4)	108.54 (25)
N(5)-Co-N(1)	95.59 (23)	O(2)-Cl(1)-O(4)	109.30 (23)
N(5)-Co-N(3)	95.34 (24)	O(5)-Cl(2)-O(8)	108.5 (4)
N(5)-Co-N(2)	94.66 (27)	O(5)-Cl(2)-O(6)	108.1 (3)
N(5)-Co-O(6)	173.73 (20)	O(5)-Cl(2)-O(7)	110.2 (3)
N(4)-Co-N(1)	93.27 (17)	O(6)-Cl(2)-O(8)	108.6 (3)
N(4)-Co-N(3)	84.94 (16)	O(7)-Cl(2)-O(8)	111.2 (3)
N(4)-Co-N(2)	171.19 (17)	O(6)-Cl(2)-O(7)	110.2 (3)
N(4)-Co-O(6)	87.91 (18)	Co-N(5)-O(9)	135.2 (11)
N(1)-Co-N(3)	169.02 (14)	Co-N(5)-O(10)	140.8 (14)
N(1)-Co-N(2)	85.06 (16)	Co-N(1)-C(1)	109.3 (3)
N(1)-Co-O(6)	90.21 (15)	Co-N(2)-C(2)	109.1 (3)
N(3)-Co-N(2)	95.05 (16)	N(1)-C(1)-C(2)	107.0 (4)
N(3)-Co-O(6)	78.91 (14)	C(1)-C(2)-N(2)	107.9 (4)
N(2)-Co-O(6)	83.45 (18)	Co-N(4)-C(4)	110.0 (3)
O(1)-Cl(1)-O(3)	109.71 (25)	Co-N(3)-C(3)	108.8 (3)
O(2)-Cl(1)-O(3)	109.87 (24)	N(4)-C(4)-C(3)	106.3 (4)
O(3)-Cl(1)-O(4)	109.13 (26)	N(3)-C(3)-C(4)	106.7 (4)
O(1)-Cl(1)-O(2)	110.25 (27)		

Table IV. Root-Mean-Square Amplitudes of Vibration (Å) in $[Co(NO)(en)_2(OClO_3)][ClO_4]$

Atom	Min	Intermed	Max
Co	0.158 (1)	0.175 (1)	0.189 (1)
Cl(1)	0.181 (2)	0.189 (2)	0.232 (2)
Cl(2)	0.162 (2)	0.181 (2)	0.209 (2)
O(1)	0.202 (6)	0.278 (5)	0.332 (5)
O(2)	0.190 (5)	0.284 (5)	0.318 (5)
O(3)	0.190 (6)	0.283 (5)	0.310 (5)
O(4)	0.204 (6)	0.257 (5)	0.333 (6)
O(5)	0.174 (7)	0.295 (6)	0.474 (7)
O(6)	0.162 (6)	0.238 (6)	0.438 (6)
O(7)	0.189 (6)	0.243 (5)	0.360 (5)
O(8)	0.193 (6)	0.280 (6)	0.470 (7)
N(1)	0.164 (7)	0.203 (6)	0.237 (6)
N(2)	0.179 (6)	0.193 (6)	0.241 (6)
N(3)	0.162 (7)	0.193 (5)	0.213 (6)
N(4)	0.156 (6)	0.231 (6)	0.248 (6)
N(5)	0.179 (9)	0.263 (7)	0.322 (8)
C(1)	0.165 (8)	0.228 (7)	0.270 (7)
C(2)	0.180 (8)	0.232 (7)	0.267 (7)
C(3)	0.168 (8)	0.206 (7)	0.272 (7)
C(4)	0.175 (8)	0.239 (7)	0.274 (7)
O(9)	0.169 (17)	0.276 (14)	0.383 (12)
O(10)	0.199 (17)	0.374 (18)	0.413 (15)

disordered, bent nitrosyl groups have been observed previously,[17] and it has been shown that an alternative model in which the nitrogen atom is also disordered (between two positions separated by about 0.4 Å) can fit the x-ray data equally well. However, because of the close proximity of the positions for the N atom, constraints must be imposed upon the parameters if the refinement is to be well behaved. In the earlier example[17] the disordered NO group was constrained to lie on a crystallographic twofold axis. In C no symmetry is imposed upon the cation by the space group. In order to get some indication of the range of Co–N–O angles which can be encompassed by the data, we refined the disordered NO moiety as two rigid groups of variable occupancy with fixed N–O distances of 1.15 Å (vide supra).

The results of this constrained refinement with partially overlapping disordered N atoms are shown in Figure 2b. The

Table V. Group Parameters for $[Co(NO)(en)_2(OClO_3)][ClO_4]$[a]

Group	x_c	y_c	z_c	ϕ	θ	ρ
N(5)-O(9)	−0.1680 (12)	0.1174 (5)	0.3686 (7)	−2.649	−2.094 (16)	1.034 (13)
N(6)-O(10)	−0.1204 (13)	0.0988 (7)	0.3875 (10)	1.183	−2.521 (20)	2.086 (17)

[a] ϕ, θ, and ρ given in radians.

Table VI. Derived Parameters for Nitrosyl Group Atoms for $[Co(NO)(en)_2(OClO_3)][ClO_4]$

Group	Atom	x	y	z	B, Å^2
N(5)-O(9)	N(5)	−0.1039 (14)	0.1026 (7)	0.3647 (10)	4.55 (14)
	O(9)	−0.2321 (13)	0.1324 (6)	0.3726 (9)	7.70 (20)
N(6)-O(10)	N(6)	−0.1430 (20)	0.1221 (9)	0.3491 (12)	*a*
	O(10)	−0.0978 (18)	0.0756 (8)	0.4258 (10)	*b*

[a] Constrained to be equal to N(5). [b] Constrained to be equal to O(9).

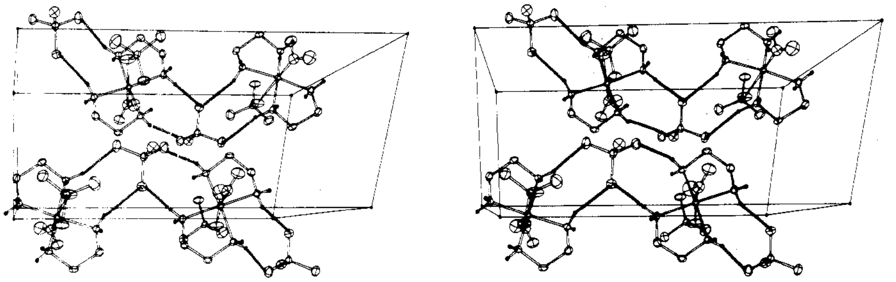


Figure 3. Stereoview of the packing for $[Co(NO)(en)_2(OClO_3)][ClO_4]$. The intermolecular hydrogen-bonding net is indicated by hatched lines. The positive direction of the *c* axis of the unit cell is up out of the plane of the paper; the positive direction of the horizontal *b* axis is toward the left. Both positions for the disordered oxygen atom of the nitrosyl group are shown.

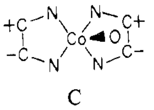
relative occupancies of the two positions are 0.56 (1) and 0.44 (1) for N(5) and N(6), respectively. The apparent separation between the two disordered N atom positions is 0.43 (2) Å.

Comparison of the molecular parameters for the two models reveals that only the distances and angles associated with the NO moiety show significant differences. The apparent separations between O(9) and O(10) in Figure 2a and b are 1.273 (15) and 1.349 (15) Å, respectively. The Co–N distance in Figure 2a of 1.806 (6) Å is not significantly different from the distances in Figure 2b of 1.805 (13) and 1.803 (17) Å. However, the choice of model does have a substantial effect on the Co–N–O angle. The model with a single anisotropic N atom (Figure 2a) gives maximum values for the Co–N–O angles (135.2 (11) and 140.8 (14)°). The constrained refinement gives a lower limit of 122° for the Co–N–O angle *provided that* 1.15 Å is a reasonable choice for the N–O distance. For comparison the $\{CoNO\}^8$ group of D appears ordered[8] and has Co–N = 1.820 (11) Å, N–O = 1.043 (17) Å, and Co–N–O = 124.4 (11)°.

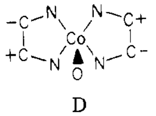
In concluding the discussion of the disorder of the NO moiety it should be noted that an *R*-factor ratio test[19] indicates that Figure 2a is significantly better that Figure 2b at the 99.5% confidence level. This result does not mean that Figure 2b is wrong and Figure 2a is correct. It does indicate, however, that there are important degrees of freedom which are constrained in Figure 2b but which are free to vary in Figure 2a. The choice of constraints for unresolved disorder is based upon chemical intuition[17,20] and the symmetry requirements of the space group.[17] For a molecule in a general position in the unit cell (such as C) there are no unique constraints for the disorder of the NO ligand. A fixed N–O distance is a reasonable constraint to impose upon C because of the limited resolution of the data (d_{min} = 1.04 Å) obtained from the small crystal.[21] Finally, we have chosen to report the detailed parameters for the model (Figure 2a) which best fits the x-ray intensity data and to summarize the significant differences between it and a chemically reasonable alternative model (Figure 2b).

The coordinated perchlorate group is trans to the NO ligand with Co–O(6) = 2.360 (4) Å. Two other examples of ClO_4^- coordinated to Co have been previously reported. In $[Co((C_6H_5)_2CH_3AsO)_4][ClO_4]_2$ the Co atom is five-coordinate with Co–O = 2.10 Å.[22] In $[Co(CH_3SCH_2CH_2SCH_3)_2][ClO_4]_2$ each Co atom is six-coordinate[23] with Co–O = 2.34 Å. The tetragonal-pyramidal $[Co(CNC_6H_5)_5]^{2+}$ ion interacts only weakly with a ClO_4^- ion in the crystal lattice[24] and has Co–O = 2.59 (1) Å. The Co–O(6) distance of C is considerably longer than 1.97 Å assumed for a Co–O single bond.[25] The long Co–O distance of C may be due to strong structural trans influence of a bent nitrosyl group[5,8] and/or the weak coordinating ability of ClO_4^-.

It is interesting to compare the conformations of the $Co(en)_2$ portions of C and D. The Co–N distances and the distances in the en ligands for the two cations are identical within experimental error. There are, however, several subtle differences in molecular geometry. In the perchlorate complex (C) the NO group bends over the en rings, while in the chloride complex (D) the NO group bends in the plane between the en rings. The relative conformations of the en rings also differ for the two ions. In C the $Co(en)_2$ fragment has approximate C_s symmetry, whereas in D the $Co(en)_2$ fragment has approximate C_2 symmetry. These differences are shown schematically below



C



D

where "+" means the C atom is above the plane of the paper and "–" means the C atom is below the plane of the paper. The N atom of the nitrosyl ligand has been omitted for clarity. It seems likely that the conformational differences observed between C and D in the solid state arise from the differences in their hydrogen-bonding networks (vide infra) rather than from inherent electronic differences in the two complexes.

The uncoordinated ClO_4^- ion of C is involved in a more extensive hydrogen-bonding network with the NH_2 groups of the en ligands than is the ClO_4^- ion in D. There are five probable interionic hydrogen bonds in C (Table VII) and all

Table VII. Possible A-H···B Hydrogen Bonds[a]

A	H	B	A···B, Å	Angle around H, deg
N(1)	H(1)	O(2)	3.12[b]	160
N(1)	H(2)	O(8)	3.07[c]	123
N(2)	H(3)	O(4)	3.06[b]	159
N(2)	H(4)	O(5)	3.07[b]	121
N(3)	H(5)	O(3)	3.10[b]	140
N(3)	H(6)	O(1)	3.16[b]	165
N(4)	H(7)	O(7)	3.13[c]	132
N(4)	H(8)	O(4)	3.02[b]	155

[a] Only interactions with A···B ≤ 3.2 Å and A-H···B > 120° are listed. [b] Interionic interaction. [c] Intraionic interaction.

four O atoms are involved in hydrogen bonding. For D there are only three strong hydrogen bonds and one of the O atoms is not involved in the network. The coordinated ClO_4^- ion of C is also involved in hydrogen bonding. Atoms O(7) and O(8) form intraionic hydrogen bonds and O(5) is involved in an interionic hydrogen bond. This extensive network of hydrogen bonds produces that rare crystallographic treat—ordered perchlorate ions. Figure 3 shows a portion of the interionic hydrogen-bonding scheme. The distances and angles in the perchlorate ions are summarized in Tables II and III.

In summary, this work has shown that C adopts six-coordinate geometry in the solid state by stabilizing the weakly bound ClO_4^- ligand via hydrogen bonding with the en ligands coordinated to cobalt. Thus, there is still no well documented example of a ligand system that produces both five- and six-coordinate $\{CoNO\}^8$ complexes with tetragonal geomtry about a strongly bent CoNO group. However, it may still be possible to isolate the five-coordinate $[Co(NO)(en)_2]^{2+}$ cation by using large counterions which cannot form hydrogen bonds and do not usually serve as ligands in metal complexes.

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Registry No. $Co(NO)(en)_2(ClO_4)_2$, 60384-76-1.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 1974 spring meeting of the American Crystallographic Association: J. H. Enemark and R. D. Feltham, Abstracts, Spring 1974 Meeting, American Crystallographic Association, Vol. 2, p 107.

(2) The superscript 8 in $\{CoNO\}^8$ refers to the total number of electrons that are primarily associated with metal d and π^*(NO) orbitals. For a more thorough discussion see ref 3 and 4.

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(6) Ligand abbreviations used in this paper: das, *o*-phenylenebis(dimethylarsine); en, ethylenediamine; dtc, diethyldithiocarbamate.

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Structure of Bis(2-thiouracil)chlorocopper(I) Dimethylformamide Solvate, a Reaction Product of Copper(II) Chloride with Thiouracil

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The structure of bis(2-thiouracil)chlorocopper(I) dimethylformamide solvate has been solved and refined by full-matrix least squares to a final convention residual of 0.055. The structure consists of almost planar molecular units of bis(2-thiouracil)chlorocopper(I) with the molecules of solvation occupying a cavity. Base stacking and hydrogen bonding also contribute to the stability of the crystal structure. The Cu(I) moiety is three-coordinate planar with two sulfurs and one chlorine coordinated to the metal. The Cu–S and Cu–Cl distances are 2.228 (1), 2.225 (1), and 2.260 (1) Å, respectively. Crystal data are as follows: $a = 12.165$ (3) Å, $b = 11.362$ (4) Å, $c = 14.565$ (4) Å, $\beta = 122.99$ (2)°, $Z = 4$, space group $P2_1/c$, $d_{\text{measd}} = 1.68$ g cm^{-3}, $d_{\text{calcd}} = 1.64$ g cm^{-3}; number of observed reflections 2902.

Introduction

The interaction between the minor base of the nucleic acids 2-thiouracil and Cu^{2+} and Cu^+ is of considerable biological interest for several reasons. Thiouracils are minor components of tRNA in both *Escherichia coli* and mammalian tissue[1-3] and the interaction of metal ions with tRNA is of importance in protein synthesis and consequently cell growth.[4,5] In addition, derivatives of 2-thiouracils are the drugs of choice in the treatment of hyperthyroid conditions[6] and elevated copper levels are observed in conjunction with these conditions.[7,8] Copper has been implicated in thyroid function at the level of iodine production,[9] the same level at which the thiouracil is thought to function. Hence, removal of cupric or cuprous ion by complexation could be an alternate possible mode of