triphenylphosphine of 1.828 ± 0.005 Å[39]). The phenyl rings are planar (see Table V) with average C–C distances of 1.391 and 1.403 Å in the two rings. The individual distances are given in Table IV. The C–C and C–N distances and the various angles in the ligand chain are close to the expected values.

The packing of the molecules in the unit cell is illustrated in Figure 2. The closest intermolecular approach to a palladium atom is 3.65 Å from a terminal sulfur atom of an isothiocyanate group. There are six other intermolecular contacts less than 3.6 Å which can be viewed as van der Waals contacts or slightly longer (see Table VIII). The slight bends at C1 and C2 of the thiocyanate groups may be related to crystal packing. A similar explanation is given for similar bends observed in the other thiocyanate complexes (see Table VI) since there are no apparent electronic reasons for deviations from linearity.

TABLE VIII

INTERMOLECULAR CONTACT DISTANCES SHORTER THAN 3.6 Å

Atom (at x, y, z)	Atom	Position[a]	Distance, Å	Atom (at x, y, z)	Atom	Position[a]	Distance, Å
S1	C11	−2	3.535	N3	C16	−2	3.498
N3	C4	−1	3.522	C2	C6	2	3.455
N3	C15	−2	3.492	C18	C18	−1	3.528

[a] The equivalent transformations are represented by: 1 for x, y, z; 2 for $x, {}^1/_2 - y, {}^1/_2 + z$; −1 for $-x, -y, -z$; −2 for $-x, {}^1/_2 + y, {}^1/_2 - z$.

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The Crystal and Molecular Structure of *trans*-Chloronitrosylbis(ethylenediamine)cobalt(III) Perchlorate

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The crystal structure of *trans*-$[CoCl(NO)(C_2H_8N_2)_2][ClO_4]$, *trans*-chloronitrosylbis(ethylenediamine)cobalt(III) perchlorate, has been determined by single-crystal X-ray diffractometry at 20°. This complex crystallizes in the monoclinic space group $P2_1/c$ with a = 6.636 (1) Å, b = 16.003 (2) Å, c = 12.315 (2) Å, and β = 103.74 (2)°. The structure, including hydrogen atoms, has been refined by least-squares techniques to an unweighted R factor of 0.062. The cobalt atom in *trans*-$CoCl(NO)(en)_2^+$ is in a distorted octahedral environment formed by the four nitrogen atoms of the ethylenediamine ligands, a chlorine atom, and the nitrogen atom of the NO group. The bent Co–N–O angle of 124.4 (11)° suggests that this complex contains a formally coordinated NO^- group. The unusually long Co(III)–Cl distance of 2.575 (3) Å indicates that the NO^- ligand exerts a large structural trans influence which is attributed to its strong σ-donor and weak π-acceptor capacity. In the crystal structure of this complex, there are hydrogen bonds between the ethylenediamine ligands and the oxygen atoms of the ClO_4^- ions.

Introduction

Because of its electronic structure NO is a versatile ligand.[1] The majority of nitrosyl complexes are thought to involve σ donation from NO^+ to the transition metal and an appreciable amount of metal→ligand π back-bonding. This group of nitrosyl compounds is characterized by a linear M–N–O group, a contracted M–N bond length, and an N–O infrared stretching frequency which is usually in the 1750–2000-cm^{-1} range.

However, examples[2-4] of complexes containing an NO^- group have recently been prepared and found to have several common physical and structural features. The N–O frequencies are in the region of ~1500–1750 cm^{-1} and the electronic spectra and magnetic susceptibility indicate an oxidation state of the metal consistent with the presence of a formally coordinated NO^- group. Moreover, an M–N–O angle of approximately 120° has been found in the two X-ray structural investigations[5,6] of this type of nitrosyl. These data suggest that the nitrogen atom of coordinated NO^- is sp^2 hybridized and that less π bonding of the metal-to-ligand type occurs than in complexes involving NO^+.

In order to determine the structural parameters associated with a bonded NO^- group we undertook a study of *trans*-$[CoCl(NO)(en)_2][ClO_4]$ where en is ethylenediamine. This complex is the first six-coordinate compound of this type which has been studied by X-ray methods, and an unexpectedly large structural trans influence of the NO^- ligand was found. The preliminary results of this study were reported earlier.[7]

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Collection and Reduction of the X-Ray Data

trans-$[CoCl(NO)(en)_2][ClO_4]$ was prepared by the method of Nyholm and Feltham.[8] Well-formed reddish brown crystals were obtained from a cold saturated aqueous solution in approximately 20 min. Precession and Weissenberg photographs showed the following absences indicative of the space group $P2_1/c$ (no. 14, C_{2h}^5): $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$. Unit cell parameters were determined by least-squares treatment of 2θ values for 16 reflections, $55 < 2\theta < 99°$, centered on a GE XRD-5 diffractometer using Cu $K\bar{\alpha}$ radiation (λ 1.5418 Å) and a takeoff angle of 2°. The cell dimensions determined were $a = 6.636$ (1), $b = 16.003$ (2), $c = 12.315$ (2) Å, and $\beta = 103.74$ (2)°. A crystal density of 1.80 (1) g/cm^3 was measured by flotation in a carbon tetrachloride–methyl iodide solution. The calculated density is 1.80 g/cm^3 for four molecules in the unit cell.

Intensity data were collected at 20° on a hexagonal prismatic crystal mounted with its a^* axis parallel to the φ axis of a GE XRD-5 diffractometer. The hexagonal faces of the crystal were (100) and ($\bar{1}$00) while the six rectangular faces were $\{011\}$ and $\{010\}$. Two parallel pairs of the hexagonal edges were 0.058 mm in length and were separated by 0.14 mm while the other parallel pairs ((010) and (0$\bar{1}$0)) were 0.11 mm long and separated by 0.094 mm. The height of the hexagonal prism was 0.30 mm. Mosaicity of the crystal was examined by the ω-scan technique using a takeoff angle of 4°. The kinematic intensity profile[9] for several reflections had a width at half-maximum intensity of approximately 0.40°.

Intensities were collected by the θ–2θ scan technique using a scan rate of 1°/min. Mo $K\alpha$ radiation filtered through either 2 mils (low-order reflections) or 1 mil of Nb foil was used with the width of the pulse height analyzer set to accept about 95% of the radiation when centered on the Mo $K\alpha$ peak. A symmetric scan range of 2° was used for all reflections and stationary-crystal, stationary-counter background counts of 20 sec each were taken at the ends of the scan range. Alignment and quality of the crystal were monitored by two standards with χ values of 0 and 59°. The intensity data were put on a common scale using these two standards. A maximum intensity variation of ±5%, which showed no systematic trend, was observed during data collection.

The 1671 independent reflections for $2\theta_{\mathrm{Mo}K\alpha} \leq 45°$ [$(\sin \theta)/\lambda \leq 0.54$)] were collected. Values of F^2 were obtained after correction of the raw intensities for background, Lorentz, polarization, and absorption effects. Standard deviations were assigned each reflection by use of the formula

$$\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (PI)^2]^{1/2}$$

where C is the total integrated count in time t_c, t_b is the time required for each background count B_1 and B_2, P is a factor introduced to correct for random fluctuations present during data collection, and I is the net integrated intensity. A value of 0.045 was chosen for P. By use of the criterion $I > 2.0\sigma(I)$, 1155 reflections were classified as observed and used in the solution and refinement of the structure. For Mo $K\alpha$ radiation the linear absorption coefficient $\mu = 18.4$ cm^{-1} and the transmission coefficients ranged from 0.76 to 0.85 for the crystal. The absorption corrections were calculated using a modified version of Coppens' program[10] which evaluates the absorption integral by the numerical method of Gauss.

Solution and Refinement of the Structure

From a three-dimensional Patterson function, the cobalt and chlorine atoms in the cation were located. A structure factor calculation phased on these two atoms gave a value of 37% for the usual agreement factor. A Fourier synthesis phased on these two atoms showed the locations of the remaining Cl, N, and O atoms. Four cycles of full-matrix least-squares refinement in which all 17 atoms were assigned isotropic temperatures led to an R_1 of 11.3% and an R_2 of 13.4%. All full-matrix least-squares refinements were carried out on F, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The usual agreement factors were defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

When all atoms were assigned anisotropic temperature factors and three more cycles of least-squares refinement of all parameters were calculated, the values of R_1 and R_2 decreased, respectively, to 0.077 and 0.092. These structure factors were used to phase a difference Fourier synthesis which showed 16 peaks ($\Delta\rho = 0.4$–0.6 $e^-/Å^3$) in reasonable locations for hydrogen atoms and a peak of height 0.8 $e^-/Å^3$ near atom O(4) of the perchlorate ion. In order to examine the perchlorate and nitrosyl group regions, least-squares calculations were performed in which all atom positional parameters were varied and all but the five oxygen and sixteen hydrogen atoms were allowed to vibrate anisotropically. Inspection of a difference electron density map at this stage revealed that the two highest peaks (1.0 and 0.8 $e^-/Å^3$) were within 1.0 Å of atom O(4) and the next peak of height 0.7 $e^-/Å$ was approximately 0.9 Å from the nitrosyl oxygen atom. None of these peaks corresponded to a chemically reasonable geometry for a disordered perchlorate or nitrosyl group. A structure factor calculation and a difference Fourier synthesis, which excluded contributions from atoms N(5) and O(5), were computed as a final test of disorder in the N–O region. No residual peaks were discernible on this difference Fourier map in the vicinity of the N–O group.

All positional and anisotropic thermal parameters were varied in three final cycles of least-squares refinement which converged to give values for the agreement factors of $R_1 = 0.062$ and $R_2 = 0.068$. (The isotropic

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) FOR $[CoCl(NO)(C_2H_8N_2)_2][ClO_4]$

K	L	FOBS	FCAL
H = 0**			
0	-2	261	225
0	4	512	508
0	6	655	677
0	10	320	306
0	12	129	170
1	12	137	117
1	11	121	120
1	10	347	323
1	9	258	247
1	8	751	780
1	7	455	471
1	6	645	643
1	4	204	198
1	3	741	731
1	2	1309	1221
1	1	517	494
2	0	1452	1320
2	1	240	225
2	2	1323	1237
2	3	614	619
2	4	199	221
2	6	229	233
2	8	166	194
2	9	180	178
2	10	210	201
2	11	99	28
2	12	94	59
3	11	172	151
3	10	181	179
3	8	993	1010
3	7	411	451
3	6	367	350
3	5	127	117
3	4	751	741
3	3	317	361
3	2	551	566
3	1	128	128
4	0	662	669
4	1	1346	1265
4	2	691	694
4	3	301	307
4	4	450	473
4	5	141	148
4	6	231	246
4	7	117	140
4	8	97	103
4	9	311	313
4	10	220	189
4	11	161	148
5	12	157	172
5	11	267	241
5	10	402	399
5	8	354	362
5	6	587	631
5	5	438	429
5	4	292	268
5	1	559	507
6	0	1333	1303
6	1	492	469
6	2	551	556
6	3	400	400
6	4	270	256
6	5	177	158
6	6	453	474
6	7	305	323
6	9	333	305
6	11	117	110
6	12	99	37
7	11	114	64
7	10	136	147
7	9	414	417
7	8	329	336
7	7	450	501
7	6	262	282
7	5	147	129
7	4	307	303
7	3	533	561
7	1	1150	1096
8	0	198	217
8	1	654	653
8	2	836	834
8	3	900	906
8	4	88	26
8	7	444	424
8	9	280	272
9	8	279	282
9	7	146	148
9	6	142	167
9	5	491	503
9	4	255	236
9	1	553	560
10	0	191	209
10	1	400	426
10	2	229	239
10	3	206	215
11	5	150	164
10	7	380	355
10	8	163	146
10	9	250	249
11	7	117	137
11	6	477	493
11	5	419	428
11	2	212	204
11	1	328	349
12	0	128	129
12	1	111	86
12	3	538	545
12	4	192	185
12	5	170	154
12	7	124	158
12	9	188	184
13	7	187	188
13	6	118	107
13	5	194	199
13	4	166	166
13	2	143	142
13	1	260	263
14	0	275	256
14	1	91	84
14	2	210	206
14	3	167	179
14	6	205	184
14	7	172	162
15	6	100	73
15	5	207	226
15	4	100	118
15	2	185	173
15	1	127	178
16	1	142	164
16	4	213	195
17	2	210	214
17	1	123	150
H = 1**			
17	0	254	252
16	3	125	155
16	2	121	91
16	1	103	127
16	0	115	119
16	-2	237	221
15	-6	104	105
15	-4	92	45
15	-3	168	222
15	-2	129	112
15	-1	103	82
15	0	167	169
15	1	164	163
15	3	262	239
15	4	198	180
14	5	101	100
14	4	273	302
14	3	139	164
14	2	277	294
14	1	263	166
14	0	137	123
14	-1	104	85
14	-4	234	228
14	-5	186	193
14	-7	222	213
13	-7	174	165
13	-4	173	96
13	-2	184	179
13	0	213	87
13	1	429	403
13	2	116	110
13	4	116	113
13	5	192	64
13	7	109	97
12	7	175	162
12	6	138	97
12	5	242	260
12	4	125	79
12	3	105	91
12	2	105	64
12	0	128	102
12	-2	214	207
12	-7	448	352
12	-8	117	41
11	-8	109	109
11	-6	105	39
11	0	172	174
11	1	587	606
11	2	103	148
11	3	381	377
11	8	124	138
10	9	285	271
10	5	124	111
10	4	329	294
10	3	549	566
10	2	239	224
10	1	387	430
10	0	146	115
10	-1	211	242
10	-4	160	118
10	-5	501	505
10	-6	135	113
10	-8	223	75
9	-8	127	135
9	-6	414	428
9	-5	131	136
9	-3	712	701
9	-1	133	127
9	1	650	669
9	2	102	53
9	3	450	442
9	4	210	218
9	6	178	182
9	7	399	422
9	10	184	187
8	9	257	270
8	6	134	155
8	5	481	513
8	4	406	421
8	3	347	341
8	2	124	98
8	0	388	421
8	-1	818	818
8	-2	222	227
8	-4	108	135
8	-5	436	411
8	-6	110	95
8	-7	467	487
7	-8	190	238
7	-7	353	354
7	-6	217	224
7	-5	547	579
7	-3	588	582
7	-2	294	258
7	0	530	554
7	1	651	647
7	2	113	95
7	3	650	671
7	4	88	95
7	5	476	477
7	7	139	150
7	9	214	208
7	10	288	261
7	11	179	161
6	11	128	125
6	9	274	277
6	8	208	206
6	7	252	294
6	6	134	108
6	5	259	263
6	3	413	402
6	2	907	918
6	0	423	415
6	-1	778	788
6	-4	444	580
6	-5	400	438
6	-6	151	167
6	-7	451	470
6	-8	136	147
5	-8	527	545
5	-7	139	168
5	-6	573	551
5	-4	348	359
5	-3	341	353
5	-1	240	221
5	1	740	708
5	2	323	328
5	3	278	285
5	4	126	85
5	6	261	223
5	7	371	401
5	8	391	418
5	10	183	216
4	11	202	192
4	9	305	339
4	8	316	318
4	6	279	284
4	5	245	222
4	4	315	311
4	3	318	324
4	2	811	791
4	1	1145	1120
4	0	446	437
4	-1	649	613
4	-4	146	135
4	-5	370	365
4	-7	255	260
4	-8	281	262
4	-11	140	108
4	-12	323	177
3	-12	127	328
3	-7	136	118
3	-6	1073	1082
3	-5	277	267
3	-4	273	246
3	-3	84	72
3	-2	924	869
3	-1	275	256
3	0	653	581
3	1	382	341
3	3	660	642
3	4	806	809
3	5	217	215
3	7	283	259
3	8	192	197
3	10	687	625
3	12	116	73
2	12	158	126
2	8	284	296
2	7	144	125
2	6	434	439
2	5	543	549
2	3	376	347
2	2	752	725
2	1	904	895
2	0	1266	1123
2	-1	923	881
2	-2	1032	956
2	-3	630	631
2	-4	247	224
2	-5	254	288
2	-6	273	277
2	-7	490	517
2	-8	296	332
2	-12	347	297
1	-12	185	201
1	-11	110	117
1	-8	653	681
1	-7	119	161
1	-6	535	566
1	-3	431	434
1	-2	1409	1328
1	-1	289	264
1	0	1218	1119
1	1	569	534
1	2	88	28
1	3	459	474
1	4	767	758
1	6	177	174
1	8	484	496
1	9	143	140
1	10	265	261
1	12	161	164
0	8	249	275
0	6	501	501
0	4	302	306
0	2	2334	2179
0	-4	1530	1449
0	-6	266	258
0	-8	318	305
H = 2**			
0	-12	523	519
0	-10	138	170
0	-6	301	298
0	-4	933	914
0	-2	1359	1370
0	0	466	443
0	2	449	453
0	4	1321	1379
0	6	168	168
0	8	213	190
0	10	196	170
1	11	175	158
1	10	273	278
1	9	99	85
1	6	439	456
1	5	142	116
1	4	254	256
1	2	447	418
1	1	560	529
1	0	82	63
1	-1	957	922
1	-2	549	566
1	-3	782	776
1	-4	1716	1651
1	-5	204	219
1	-6	942	968
1	-7	204	200
1	-8	293	300
1	-9	281	288
1	-10	285	278
1	-12	164	170
2	-13	108	71
2	-12	327	328
2	-10	461	424
2	-9	129	129
2	-8	78	23
2	-7	85	27
2	-6	503	505
2	-5	425	424
2	-4	578	569
2	-3	250	258
2	-1	316	291
2	0	291	277
2	1	88	63
2	2	1110	1087
2	3	405	409
2	4	1236	1270
2	5	137	138
2	6	329	319
2	7	133	140
2	8	270	255
3	10	223	232
3	9	211	198
3	6	539	545
3	5	219	223
3	4	292	307
3	3	391	415
3	2	281	282
3	1	425	435
3	0	538	532
3	-1	146	145
3	-3	516	501
3	-4	1084	1147
3	-5	196	191
3	-6	247	252
3	-7	164	172
3	-8	143	144
3	-12	123	136
4	-12	333	340
4	-11	232	238
4	-10	307	306
4	-8	133	136
4	-7	170	169
4	-6	91	81
4	-5	342	375
4	-4	435	338
4	-1	229	239
4	1	170	94
4	2	632	624
4	3	662	662
4	4	747	768
4	5	418	442
4	6	306	320
4	7	80	81
4	8	189	199
4	10	159	150
4	11	240	221
5	10	300	290
5	9	232	240
5	8	91	113
5	7	216	213
5	6	145	147
5	5	221	244
5	4	273	295
5	3	418	427
5	2	174	167
5	1	132	122
5	-1	121	134
5	-2	639	658
5	-4	449	435
5	-6	599	644
5	-7	504	531
5	-8	181	194
5	-9	115	130
5	-10	268	276
5	-11	141	128
6	-11	135	117
6	-9	391	365
6	-5	673	694
6	-4	228	228
6	-3	257	293
6	-2	478	507
6	0	136	114
6	1	575	573
6	2	105	100
6	4	715	750
6	5	253	262
6	6	95	99
6	7	299	226
6	8	116	112
6	9	201	178
6	10	126	130
7	10	134	139
7	9	86	47
7	7	208	216
7	6	115	133
7	5	310	316
7	3	597	607
7	2	265	281
7	1	91	105
7	0	84	142
7	-1	193	193
7	-2	352	337
7	-3	538	565
7	-4	461	486
7	-5	261	276
7	-6	361	387
7	-7	218	231
7	-8	129	131
7	-9	192	136
7	-10	159	161
7	-11	243	228
8	-11	167	168
8	-10	272	262
8	-9	295	301
8	-8	92	75
8	-6	167	141
8	-5	608	606
8	-4	139	144
8	-3	389	361
8	-2	200	190
8	-1	100	101
8	0	374	404
8	1	594	570
8	2	674	696
8	3	140	147
8	4	138	140
8	5	357	337
8	6	420	439
8	7	174	172
8	8	93	111
8	9	94	34
9	8	279	276
9	7	107	68
9	2	192	157
9	1	140	140
9	-1	618	630
9	-2	440	483
9	-3	234	276
9	-4	327	348
9	-7	488	498
9	-10	130	91
9	-11	177	159
10	-10	121	125
10	-9	224	214
10	-5	398	407
10	-1	211	208
10	0	263	235
10	1	371	373
10	2	279	291
10	3	372	388
10	4	159	141
10	5	372	435
10	8	104	85
11	7	99	91
11	5	179	184
11	4	81	45
11	2	432	418
11	-1	349	377
11	-2	390	367
11	-3	187	211
11	-4	137	114
11	-6	260	248
11	-7	278	284
12	-9	339	320
12	-7	143	155
12	-4	231	233
12	-3	143	123
12	0	217	214
12	1	464	466
12	3	122	121
12	7	244	251
13	6	100	85
13	5	109	126
13	3	239	238
13	1	85	69
13	0	238	222
13	-1	120	149
13	-3	265	240
13	-4	140	136
13	-5	107	79
13	-6	103	139
13	-7	127	111
13	-8	179	179
14	-6	188	182
14	-5	151	154
14	-3	188	171
14	-2	105	86
14	1	158	168
14	3	139	136
14	5	192	145
15	3	179	158
15	2	105	129
15	0	196	201
15	-1	267	275
15	-6	88	63
16	-3	138	129
16	-2	155	178
16	0	200	213
16	1	114	86
16	2	182	174
H = 3**			
15	-4	95	73
15	-3	96	108
15	1	244	224
14	3	112	87
14	-1	231	202
14	-3	244	253
14	-4	139	142
13	-6	164	143
13	-4	118	91
13	-3	160	146
13	-2	116	118
13	-1	325	322
13	2	115	130
13	3	166	78
13	4	89	73
13	5	297	289
12	2	131	124
12	1	89	152
12	-1	224	218
12	-3	297	302
12	-5	120	121
12	-6	204	198
12	-7	283	230
11	-9	200	197
11	-7	128	120
11	-6	127	71
11	-5	179	184
11	-2	149	124
11	-1	307	320
11	0	106	68
11	1	212	191
11	4	154	148
11	5	320	318
10	7	331	325
10	6	107	129
10	5	152	157
10	3	183	177
10	2	262	246
10	1	192	189
10	-1	332	321
10	-3	540	518
10	-6	183	168
10	-7	235	238
10	-9	327	328
10	-10	208	197
9	-9	219	224
9	-8	98	133
9	-5	563	571
9	-3	248	272
9	-2	352	315
9	-1	288	285
9	0	191	185
9	1	596	614
9	2	105	95
9	3	189	212
9	4	196	138
9	5	366	372
9	7	208	191
9	8	84	49
8	8	104	117
8	7	109	121
8	4	335	327
8	3	479	488
8	2	213	218
8	1	144	139
8	0	156	143
8	-1	231	221
8	-2	161	160
8	-3	574	601
8	-4	87	77
8	-5	166	165
8	-6	205	179
8	-7	483	510
8	-8	188	186
8	-9	237	223
8	-10	102	88
7	-11	207	186
7	-10	118	129
7	-9	269	248
7	-8	231	226
7	-7	176	158
7	-6	105	88
7	-5	267	268
7	-4	399	389
7	-2	524	550
7	-1	547	562
7	0	179	142
7	1	174	186
7	2	122	85
7	4	139	144
7	5	428	432
7	7	121	115
1	3	100	120
1	4	217	213
1	5	91	99
1	6	97	89
1	7	110	118
1	8	184	208
0	10	95	66
0	6	401	416
0	4	405	415
0	2	336	341
0	0	622	625
0	-4	585	588
0	-6	441	443
0	-8	82	78
0	-10	391	387
0	-12	198	178
7	8	129	99
6	9	189	180
6	7	131	133
6	6	535	504
6	5	129	138
6	3	425	439
6	2	89	48
6	1	89	97
6	0	209	219
6	-1	175	174
6	-2	137	133
6	-3	459	463
6	-5	72	41
6	-6	120	88
6	-7	418	425
6	-9	167	139
6	-10	226	281
6	-12	132	108
5	-11	161	169
5	-10	167	172
5	-9	234	241
5	-8	196	192
5	-6	135	118
5	-5	372	387
5	-4	536	556
5	-2	267	219
5	-1	320	317
5	0	576	575
5	1	368	371
5	2	158	160
5	3	272	273
5	4	232	234
5	5	277	305
5	6	96	54
5	7	124	116
5	8	207	198
5	9	91	90
4	8	104	93
4	7	371	364
4	6	536	576
4	5	109	108
4	4	443	459
4	2	151	133
4	1	148	159
4	0	295	293
4	-1	307	320
4	-2	90	112
4	-3	557	575
4	-4	100	94
4	-6	168	196
4	-7	187	183
4	-8	260	273
4	-10	411	418
4	-12	224	273
3	-12	183	93
3	-11	109	111
3	-10	104	106
3	-8	548	528
3	-7	98	82
3	-6	135	135
3	-5	271	263
3	-4	417	386
3	-3	154	145
3	-2	843	872
3	0	215	219
3	1	447	450
3	2	208	174
3	4	383	386
3	5	301	321
3	6	308	319
3	7	189	205
3	8	259	269
2	10	249	241
2	9	244	232
2	8	189	156
2	7	172	144
2	6	381	411
2	4	742	738
2	3	282	287
2	2	239	234
2	0	543	621
2	-1	476	488
2	-2	302	292
2	-4	367	355
2	-5	242	248
2	-6	365	365
2	-7	164	176
2	-8	392	394
2	-9	79	56
2	-10	339	341
2	-11	221	211
2	-12	271	274
1	-10	219	228
1	-8	436	423
1	-7	112	101
1	-6	363	360
1	-5	131	109
1	-4	927	946
1	-2	842	792
1	-1	264	270
1	0	457	449
1	1	175	176
1	2	694	717
H = 4**			
0	-10	184	185
0	-8	819	762
0	-6	161	135
0	-4	97	91
0	-2	566	566
0	0	655	685
0	2	624	620
0	4	81	72
0	6	210	199
0	8	563	534
1	8	210	198
1	7	171	129
1	6	94	58
1	5	207	208
1	4	172	105
1	2	300	291
1	1	399	422
1	0	891	886
1	-1	364	367
1	-2	695	726
1	-3	127	123
1	-4	103	87
1	-5	172	86
1	-6	604	612
1	-8	437	425
2	-10	395	397
2	-8	453	462
2	-6	328	317
2	-4	279	288
2	-3	92	108
2	0	537	524
2	1	231	241
2	2	410	414
2	4	128	92
2	6	265	257
3	8	208	208
3	7	119	136
3	3	217	235
3	2	141	154
3	1	152	169
3	0	748	745
3	-2	359	379
3	-5	95	92
3	-6	577	524
3	-8	320	313
3	-9	200	201
4	-11	89	82
4	-10	256	252
4	-9	86	102
4	-8	347	336
4	-7	464	448
4	-6	384	413
4	-4	141	143
4	-3	127	123
4	-2	142	142
4	-1	423	407
4	0	247	301
4	1	124	127
4	2	399	419
4	3	295	292
4	4	103	101
4	6	371	370
4	7	123	115
4	8	280	271
5	8	90	80
5	7	194	205
5	5	242	234
5	4	214	233
5	3	244	242
5	2	459	478
5	1	82	86
5	0	127	114
5	-1	81	50
5	-2	501	516
5	-3	333	329
5	-4	273	315
5	-5	95	70
5	-6	242	233
5	-7	113	171
5	-8	222	220
5	-9	177	224
5	-10	125	130
6	-11	205	204
6	-8	324	336
6	-7	125	163
6	-5	297	307
6	-3	114	134
6	-2	84	82
6	-1	335	378
6	0	250	257
6	1	125	132
6	2	371	353
6	3	234	244
7	3	325	326
7	2	199	208
7	1	599	585
7	0	424	424
7	-1	204	198
7	-2	357	348
7	-3	185	189
7	-5	274	260
7	-6	357	369
7	-7	286	268
7	-8	161	143
7	-9	278	282
7	-10	155	176
8	-10	202	212
8	-7	230	251
8	-6	260	264
8	-5	346	372
8	-4	194	176
8	-3	268	256
8	-2	116	136
8	-1	563	578
8	0	206	207
8	1	166	177
8	2	109	91
8	3	145	142
8	4	118	107
8	5	275	264
8	6	213	224
9	5	119	140
9	4	98	151
9	3	237	255
9	1	221	246
9	0	358	266
9	-1	187	208
9	-2	104	113
9	-3	479	495
9	-4	100	99
9	-5	133	129
9	-6	159	147
9	-7	156	162
9	-8	118	104
9	-9	244	246
10	-8	182	148
10	-7	343	361
10	-6	145	166
10	-5	190	192
10	-4	103	132
10	-3	111	138
10	-2	144	156
10	-1	472	457
10	0	113	99
10	1	118	107
10	3	178	172
10	5	140	158
11	5	104	115
11	4	92	40
11	3	202	208
11	2	248	243
11	1	134	115
11	0	119	171
11	-2	144	149
11	-3	348	336
11	-5	114	112
11	-7	126	180
12	-5	338	336
12	-4	211	210
12	-3	140	118
12	-1	160	163
12	1	138	117
13	1	192	172
13	0	122	85
13	-2	131	106
13	-3	107	127
13	-4	149	137
13	-5	110	104
14	-2	138	107
14	-1	178	169
H = 5**			
12	-2	153	158
12	-3	228	217
11	-5	139	163
11	-1	174	166
11	0	103	66
10	3	150	106
10	1	328	324
10	-2	108	116
10	-3	131	137
10	-5	391	390
10	-6	157	137
9	-7	219	228
9	-6	121	93
9	-4	136	116
9	-3	158	151
9	-2	164	136
9	-1	309	311
9	1	288	233
9	2	233	287
9	3	176	148
9	4	118	126
8	3	128	87
8	1	367	367
8	-1	248	246
8	-2	144	144
8	-3	387	383
8	-4	128	118
8	-5	233	234
8	-7	178	167
8	-8	272	243
7	-8	87	108
7	-7	176	225
7	-6	196	163
7	-5	253	252
7	-4	197	178
7	-3	306	312
7	-2	81	48
7	-1	148	142
7	0	240	229
7	1	49	26
7	2	269	241
7	3	484	401
6	5	130	113
6	4	236	209
6	2	119	119
6	1	202	211
6	0	205	193
6	-1	204	202
6	-3	382	374
6	-6	332	375
6	-7	98	99
6	-8	118	112
6	-9	184	198
5	-10	105	97
5	-9	123	110
5	-7	180	172
5	-6	188	178
5	-5	114	155
5	-4	145	143
5	-2	174	173
5	-1	242	242
5	0	537	525
5	1	216	211
5	2	211	199
5	4	183	185
5	5	152	145
5	6	205	199
4	5	102	126
4	4	205	201
4	3	125	147
4	2	249	240
4	1	182	194
4	0	94	64
4	-1	45	25
4	-2	137	120
4	-4	193	199
4	-5	366	377
4	-6	301	295
4	-7	95	91
4	-8	208	231
3	-11	105	96
3	-10	83	79
3	-9	115	91
3	-7	113	168
3	-6	207	195
3	-4	381	398
3	-3	86	45
3	-2	183	186
3	-1	214	205
3	0	259	243
3	1	181	150
3	2	534	519
3	4	82	113
3	5	210	201
3	6	87	62
2	5	105	87
2	4	168	175
2	3	132	161
2	2	252	277
2	1	198	184
2	-1	231	249
2	-2	432	444
2	-4	187	170
2	-6	272	288
2	-7	205	201
2	-8	439	428
2	-9	156	130
2	-10	107	105
1	-10	232	215
1	-9	104	34
1	-6	355	336
1	-5	108	97
1	-4	539	546
1	-3	132	124
1	0	665	641
1	1	189	196
1	2	224	248
1	3	184	200
1	4	126	124
1	6	244	252
0	4	363	369
0	2	178	194
0	0	163	199
0	-2	404	404
0	-4	130	92
0	-6	637	617
0	-8	258	260
H = 6**			
0	-6	225	219
0	-4	626	624
0	-2	131	138
0	0	132	120
0	4	272	264
1	4	221	225
1	3	135	145
1	2	371	342
1	-1	204	198
1	-2	460	452
1	-4	429	436
1	-6	81	70
1	-8	104	112
2	-7	87	89
2	-6	330	317
2	-4	248	257
2	-3	101	140
2	-2	98	94
2	-1	133	129
2	0	205	192
2	3	157	156
2	4	263	243
3	2	155	146
3	1	188	161
3	-1	103	105
3	-2	394	397
3	-4	218	216
3	-5	124	124
4	-8	91	101
4	-6	172	190
4	-5	146	138
4	-4	185	175
4	-3	259	269
4	3	155	143
5	3	131	133
5	2	298	307
5	1	152	139
5	0	137	149
5	-2	259	254
5	-3	91	76
5	-4	270	253
5	-5	165	201
5	-6	88	72
5	-8	109	103
6	-8	111	59
6	-7	199	193
6	-6	94	86
6	-4	269	285
6	-3	166	173
6	-1	182	180
6	1	239	231
7	0	108	82
7	-1	258	284
7	-2	183	182
7	-3	146	156
7	-4	213	209
7	-5	271	256
7	-6	134	117
7	-7	99	87
8	-6	234	216
8	-5	130	126
8	-3	245	242
8	-2	151	172
8	-1	125	126
9	-1	152	152
9	-2	105	98
H = 7**			
3	-3	88	79
3	-2	169	153
2	-3	117	113
1	-4	101	58
2	-4	287	272
1	-2	227	235
0	-2	239	229
0	-4	252	264

thermal parameters of the hydrogen atoms were not varied but were assigned B values one unit greater than those for the atoms to which they were bonded.) During the last cycle of refinement the maximum change of a positional or thermal parameter for a nonhydrogen atom was 0.2σ and the average change was about 0.03σ. The two highest peaks of 0.7 and 0.6 $e^-/Å^3$ on the final difference electron density map ($\sigma(\Delta\rho) = 0.13$ $e^-/Å^3$) were in the vicinity of atom O(4) of the perchlorate group. At the completion of the structural analysis the error of an observation of unit weight was 2.08.

Past X-ray determinations of nitrosyl structures usually have assumed that the N atom of the N–O group has been bonded to the metal atom. In a few studies[5,11] analysis of the thermal ellipsoids with the N and O atoms form factors reversed has shown that the M–N–O structure is the more reasonable one. In order to clarify which atom was attached to Co in this structure, a structure factor calculation was performed in which the scattering factor used for atoms N(5) and O(5) was the N atom core[12] scattering factor. The difference Fourier map phased on these structure factors showed, as would be predicted, that the N atom bonded to Co had a valence electron density peak height (2.42 $e^-/Å^3$) less than that of the O(5) atom (2.47 $e^-/Å^3$) although it was initially anticipated that the peak height differences for these two atoms would be greater. However, thermal bias on Fourier difference maps[13] is known to be particularly severe at the nuclear positions. Since the O(5) atom, with an isotropic thermal parameter of 9.0 $Å^2$, undergoes greater thermal motion than the N(5) atom ($B = 4.8$ $Å^2$), a reduction in the peak height of the former atom is expected. Moreover, examination of this difference map shows that the valence electron density decreases more slowly for the oxygen than the nitrogen atom as one moves away from their respective nuclear positions It is difficult to interpret these observations as being consistent with an arrangement other than a Co–N–O linkage.

The major programs used in the solution of this structure were Zalkin's FORDAP for Patterson and Fourier synthesis and Prewitt's SFLS-5 structure factor calculations and least-squares refinement. Corrections for the real and imaginary components of anomalous dispersion[14] were applied to the cobalt[15] and chlorine atom scattering factors. Hydrogen scattering factors were those of Stewart, *et al.*,[16] and all other light atom scattering factors were those of the neutral atoms given by Ibers.[17]

The amplitudes, $10|F_o|$, and the final calculated structure factors, $10F_c$, are given for the observed reflections in Table I. The 516 unobserved reflections

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(11) G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970).

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(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(17) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

Table II

Final Positional and Thermal Parameters for $[CoCl(NO)(C_2H_8N_2)_2][ClO_4]$

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.1672 (2)[a]	0.22578 (9)	0.4058 (1)	146 (3)	33.1 (7)	47 (1)	0 (1)	19 (1)	2.5 (8)
Cl(1)	0.9179 (4)	0.2407 (2)	0.5361 (2)	234 (8)	70 (2)	52 (2)	2 (3)	42 (3)	−12 (5)
Cl(2)	0.5630 (4)	0.4315 (2)	0.2221 (3)	245 (8)	34 (1)	76 (3)	−6 (3)	16 (3)	4 (2)
N(1)	0.9261 (14)	0.1939 (6)	0.2877 (7)	217 (24)	34 (5)	41 (7)	0 (8)	16 (11)	4 (5)
N(2)	0.1815 (13)	0.1071 (6)	0.4452 (8)	162 (22)	44 (5)	45 (8)	8 (8)	21 (11)	3 (5)
N(3)	0.3932 (14)	0.2393 (7)	0.0317 (9)	158 (24)	40 (6)	80 (9)	9 (8)	9 (11)	1 (6)
N(4)	0.1269 (14)	0.3464 (6)	0.3735 (9)	229 (26)	40 (5)	66 (9)	5 (9)	3 (13)	4 (5)
N(5)	0.3347 (16)	0.2162 (7)	0.3089 (9)	273 (30)	34 (5)	120 (11)	31 (10)	71 (14)	16 (6)
C(1)	0.9271 (19)	0.1036 (8)	0.2735 (10)	240 (34)	44 (7)	61 (10)	−29 (11)	−3 (14)	−2 (7)
C(2)	0.9924 (17)	0.0622 (8)	0.3860 (9)	261 (32)	28 (5)	56 (10)	−22 (11)	11 (13)	10 (6)
C(3)	0.4363 (20)	0.3514 (10)	0.5200 (14)	264 (40)	58 (8)	106 (14)	−36 (14)	7 (17)	−25 (9)
C(4)	0.2356 (21)	0.3948 (9)	0.4720 (13)	339 (43)	41 (7)	109 (15)	−10 (13)	23 (20)	−10 (8)
O(1)	0.5844 (19)	0.4587 (10)	0.1213 (10)	670 (47)	186 (15)	138 (13)	−194 (21)	−33 (19)	82 (11)
O(2)	0.3523 (13)	0.4123 (8)	0.2064 (9)	320 (29)	124 (9)	141 (12)	2 (12)	57 (14)	40 (7)
O(3)	0.6611 (17)	0.3572 (8)	0.2532 (11)	477 (39)	94 (9)	245 (18)	91 (14)	10 (20)	11 (10)
O(4)	0.6439 (32)	0.4843 (11)	0.3007 (14)	1463 (105)	108 (11)	245 (22)	88 (28)	25 (39)	97 (13)
O(5)	0.4653 (20)	0.1778 (8)	0.3217 (10)	581 (45)	79 (7)	200 (15)	−5 (14)	224 (21)	10 (8)
H(1)N(1)[c]	−0.062 (16)	0.2075 (9)	0.2232 (94)						
H(2)N(1)[d]	0.819 (16)	0.2167 (68)	0.3081 (86)						
H(1)N(2)	0.287 (17)	0.0786 (71)	0.4351 (88)						
H(2)N(2)	0.166 (17)	0.1018 (72)	0.507 (10)						
H(1)N(3)	0.335 (19)	0.2567 (78)	0.073 (10)						
H(2)N(3)	0.487 (18)	0.2709 (72)	0.051 (93)						
H(1)N(4)	0.154 (17)	0.3527 (75)	0.302 (10)						
H(2)N(4)	0.1007 (19)	0.3467 (80)	0.348 (10)						
H(1)C(1)	0.831 (17)	0.0822 (74)	0.232 (10)						
H(2)C(1)	0.044 (18)	0.0857 (70)	0.2366 (96)						
H(1)C(2)	0.900 (17)	0.0887 (70)	0.425 (10)						
H(2)C(2)	0.999 (17)	1.0008 (80)	0.374 (10)						
H(1)C(3)	0.478 (19)	0.1334 (81)	0.105 (11)						
H(2)C(3)	0.521 (21)	0.3486 (90)	0.484 (11)						
H(1)C(4)	0.147 (20)	0.0972 (79)	0.038 (11)						
H(2)C(4)	0.259 (18)	0.4586 (89)	0.477 (10)						

[a] The numbers in parentheses are esd's in the last figure quoted. [b] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [c] H atom thermal parameters were not refined but were assigned a B value one unit greater than the equivalent B for the carbon to which they were attached. [d] H(2)N(1) designates the second H atom attached to the N(1) atom.

were included in a terminal structure factor calculation and there were three reflections for which $|F_o|$ was greater than twice the minimum observable. Table II lists the positional and thermal parameters obtained in the last cycle of least-squares refinement. The rms amplitudes of thermal vibration and their direction cosines are given in Table III. Except for the oxygen atoms, the anisotropy of thermal motion for the atoms is small.

Results and Discussion

The crystal structure is composed of *trans*-CoCl(NO)(en)$_2^+$ cations and ClO_4^- anions. A view of the *trans*-CoCl(NO)(en)$_2^+$ ion projected down the crystallographic c axis is given in Figure 1 and the numbering scheme is included in this figure. Figure 2 shows a projection of the crystal packing down the a^* axis. Selected interatomic bond distances and angles in the structure are given in Table IV.

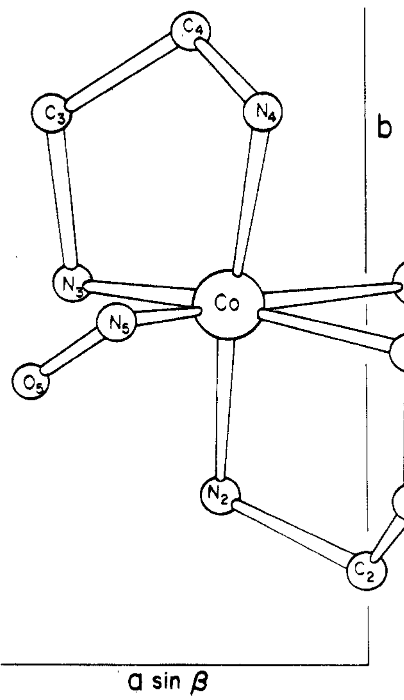

Figure 1.—The *trans*-CoCl(NO)(en)$_2^+$ ion projected down the crystallographic c axis.

In *trans*-CoCl(NO)(en)$_2^+$ four nitrogen atoms from two ethylenediamine ligands, one nitrogen atom of the NO group, and a chlorine atom form a distorted octahedral environment around the central cobalt atom. The four N atoms of the ethylenediamine groups lie very nearly in a plane and the Co atom is displaced

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) AND THEIR DIRECTION COSINES[a]

Atom	Minor axis	Medium axis	Major axis
Co	0.175 (0.988, 0.022, 0.151)	0.184 (−0.140, −0.263, 0.955)	0.209 (−0.061, 0.965, 0.256)
Cl(1)	0.176 (−0.477, 0.200, 0.856)	0.225 (0.877, 0.050, 0.477)	0.306 (0.052, 0.979, −0.199)
Cl(2)	0.205 (0.224, 0.963, −0.147)	0.219 (0.698, −0.054, 0.714)	0.251 (−0.680, 0.263, 0.684)
N(1)	0.169 (0.021, −0.264, 0.964)	0.210 (0.442, 0.867, 0.228)	0.218 (0.897, −0.421, −0.136)
N(2)	0.179 (−0.176, −0.086, 0.980)	0.183 (0.973, −0.164, 0.160)	0.240 (0.147, 0.983, 0.113)
N(3)	0.178 (0.904, −0.223, 0.366)	0.229 (0.184, 0.973, 0.139)	0.249 (−0.387, −0.058, 0.920)
N(4)	0.197 (0.573, −0.281, 0.770)	0.230 (0.262, 0.953, 0.152)	0.247 (0.777, −0.115, −0.620)
N(5)	0.181 (−0.500, 0.849, −0.171)	0.234 (0.827, 0.410, −0.386)	0.308 (0.257, 0.334, 0.907)
C(1)	0.180 (0.598, 0.412, 0.688)	0.228 (−0.325, −0.660, 0.678)	0.272 (0.733, −0.629, −0.260)
C(2)	0.160 (0.290, 0.843, −0.454)	0.202 (0.487, 0.279, 0.828)	0.262 (0.824, −0.461, −0.330)
C(3)	0.188 (0.615, 0.549, 0.566)	0.279 (0.784, −0.499, −0.369)	0.318 (−0.080, −0.671, 0.737)
C(4)	0.220 (0.228, 0.902, 0.365)	0.266 (0.777, −0.395, 0.490)	0.298 (−0.587, −0.172, 0.791)
O(1)	0.237 (−0.438, −0.585, 0.682)	0.295 (0.715, 0.233, 0.659)	0.600 (−0.544, 0.777, 0.317)
O(2)	0.255 (0.991, 0.115, −0.072)	0.288 (0.115, −0.434, 0.894)	0.426 (−0.071, 0.894, 0.443)
O(3)	0.246 (0.736, −0.607, 0.301)	0.394 (0.454, 0.772, 0.446)	0.445 (−0.503, −0.191, 0.843)
O(4)	0.229 (0.181, 0.746, 0.641)	0.499 (0.234, −0.666, 0.709)	0.598 (0.955, 0.022, −0.295)
O(5)	0.240 (0.820, 0.209, −0.533)	0.323 (−0.214, 0.975, 0.054)	0.424 (0.531, 0.070, 0.845)

[a] Direction cosines are referred to the orthogonal coordinate system *a*, *b*, *c**.

0.09 Å out of this mean plane toward the NO group. (The weighted least-squares plane through N(1), N(2), N(3), and N(4) shows that these four atoms are alternatingly above and below this plane by 0.01 Å.) A similar displacement of the central metal atom by 0.2 Å toward an NO group occurs in the $Fe(CN)_5NO^{2-}$ ion,[18] but the related species, *trans*-$RuNO(OH)(NO_2)_4^{2-}$,[19] does not show an analogous distortion. An average value of 1.964 (5) Å was determined for the four Co–N(en) distances which compares well with other Co(III)–N(sp^3) distances reported in the literature such as for $[Co(NH_3)_6]I_3$,[20] 1.936 (15) Å; *trans*-$Co(en)_2SO_3(NCS)$,[21] 1.962 (10) Å; and (+)D-$[Co(en)_3]Cl_3 \cdot H_2O$,[22] 1.978 (4) Å.

The Co–N(O) distance of 1.820 (11) Å is significantly shorter (~13σ) than the average Co–N(en) in this complex which indicates that there is some multiple character in the cobalt–nitrosyl bond. If a correction of −0.03 Å is made in going from sp^3- to sp^2-hybridized nitrogen, the shortening is approximately 0.11 Å. This contraction is not as large as that found in other nitrosyls—$Fe(CN)_5NO^{2-}$, ~0.24 Å;[18] $RuNO(S_2CN(C_2H_5)_2)_3$,[23] ~0.25 Å; $(\pi\text{-}C_5H_5)Cr(NO)_2Cl$,[24] ~0.41 Å—all of which can be formally described as having a coordinated NO^+ group. It is also apparent that within the group of complexes designated as containing an NO^+ group, the amount of contraction is greatest when the formal charge on the metal atom is smallest.

It seems reasonable that if the NO group in a nitrosyl complex can be formally described as NO^+, more back-π-donation of the metal to ligand type can occur than if the group is best depicted as NO^-. The two complexes $[IrNO(X)(CO)(P(C_6H_5)_3)_2][BF_4]$,[5,6] where X = Cl or I, are thought to contain an NO^- group and the Ir–C(O) bonds (Ir–C = 1.86 (1), 1.70 (5) Å; X = Cl, I) are significantly shorter than the Ir–N(O) bonds (Ir–N = 1.97 (1) Å, 1.89 (3) Å; X = Cl, I). Since the covalent radius of C(sp) is greater than that of N(sp^2), these relative distances were taken as evidence for the occurrence of less π back-bonding in the Ir–N(O) bond than in the Ir–C(O) bond. Some metal-to-nitrogen π bonding probably occurs as indicated by the contraction (0.09 (3) Å) of the Ir–N bond in the iodide compared to the chloride. Presumably, the iodo complex would leave the greater electron density on the metal and

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[23] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).

[24] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1095 (1966).

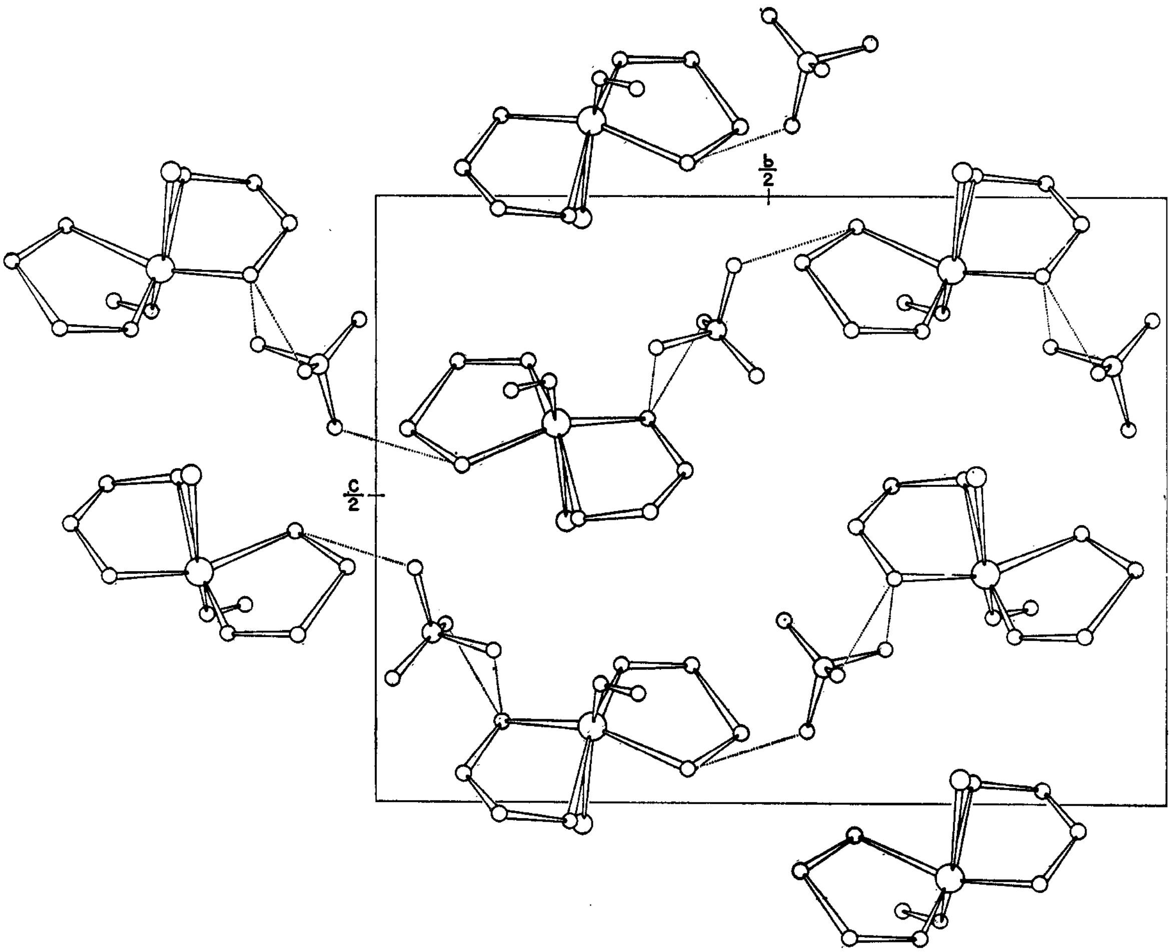

Figure 2.—The crystal packing of *trans*-$[\mathrm{CoCl(NO)(en)_2}][\mathrm{ClO_4}]$ projected on the crystallogrpahic *bc* plane. Only the hydrogen bonds with O···H distances less than 2.4 Å are indicated in the figure.

Table IV

Principal Molecular Dimensions[a]

Bond Distances, Å		Intramolecular Nonbonded Contacts, Å		Interbond Angles, Deg			
Co–N(1)	1.957 (9)	N(1)···N(2)	2.65 (1)	Co–N(5)–O(5)	124.4 (11)	Cl(1)–Co–N(4)	87.6 (3)
Co–N(2)	1.957 (10)	N(3)···N(4)	2.68 (1)	Cl(1)–Co–N(5)	177.6 (4)	Co–N(1)–C(1)	108.8 (7)
Co–N(3)	1.965 (10)	N(1)···N(4)	2.86 (1)	N(5)–Co–N(1)	90.5 (4)	Co–N(2)–C(2)	111.3 (7)
Co–N(4)	1.977 (10)	N(2)...N(3)	2.91 (1)	N(5)–Co–N(2)	94.6 (4)	Co–N(3)–C(3)	109.1 (7)
Co–N(5)	1.820 (11)	N(1)···O(5)	3.51 (2)	N(5)–Co–N(3)	94.1 (4)	Co–N(4)–C(4)	109.3 (8)
Co–Cl(1)	2.575 (3)	N(2)···O(5)	2.92 (2)	N(5)–Co–N(4)	91.4 (5)	N(1)–C(1)–C(2)	110 (1)
N(5)–O(5)	1.043 (17) [1.109][b]	N(3)···O(5)	3.04 (2)	N(1)–Co–N(2)	85.1 (4)	N(2)–C(2)–C(1)	105 (1)
C(1)–N(1)	1.46 (2)	N(4)···O(5)	3.66 (2)	N(3)–Co–N(4)	85.6 (4)	N(3)–C(3)–C(4)	108 (1)
C(2)–N(2)	1.48 (2)	N(1)···Cl(1)	3.16 (1)	N(2)–Co–N(3)	95.6 (4)	N(4)–C(4)–C(3)	107 (1)
C(3)–N(3)	1.49 (2)	N(2)···Cl(1)	3.13 (1)	N(1)–Co–N(4)	93.3 (4)	O(1)–Cl(2)–O(2)	105.3 (8)
C(4)–N(4)	1.48 (2)	N(3)···Cl(1)	3.18 (1)	N(1)–Co–N(3)	175.3 (4)	O(1)–Cl(2)–O(3)	113.0 (8)
C(1)–C(2)	1.50 (2)	N(4)···Cl(1)	3.18 (1)	N(2)–Co–N(4)	173.8 (4)	O(2)–Cl(2)–O(3)	103.9 (7)
C(3)–C(4)	1.49 (2)	Co···O(5)	2.56 (1)	Cl(1)–Co–N(1)	87.4 (3)	O(1)–Cl(2)–O(4)	111.0 (10)
Cl(2)–O(1)	1.35 (1) [1.47]			Cl(1)–Co–N(2)	86.3 (3)	O(2)–Cl(2)–O(4)	117.8 (9)
Cl(2)–O(2)	1.40 (1) [1.46]			Cl(1)–Co–N(3)	88.0 (3)	O(3)–Cl(2)–O(4)	105.8 (7)
Cl(2)–O(3)	1.37 (1) [1.44]						
Cl(2)–O(4)	1.30 (2) [1.42]						

[a] Standard deviations of least significant figures are given in parentheses. [b] Distances within brackets are corrected for thermal vibration using a riding model. For details see C. K. Johnson in "Crystallographic Computing," F. A. Ahmed, Ed., Munksgaard, Copenhagen, 1970; also W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17,** 142 (1964).

consequently more back-bonding of the type $\mathrm{Ir}\rightleftharpoons\mathrm{N}$ would occur.

Perhaps the most significant aspect of this structure is the Co–N–O angle of 124.4 (11)°. The value of this angle and the relatively small contraction (~0.11 Å) of the Co–N(O) bond relative to the Co–N single bond length indicate that the $\mathrm{NO^-}$ formalism is the more suitable one to describe the NO group in this complex.

TABLE V

STRUCTURAL TRANS INFLUENCE IN SOME SIX-COORDINATE d^6 COMPLEXES

Nitrosyls

Complex	Formalism for NO group	Ligand (X) trans to NO	M–X,[a] Å	Expected M–X,[b] Å	Trans influence lengthening, Å
$Na_2[Fe(CN)_5NO] \cdot 2H_2O$[c]	NO^+	CN^-	1.90 (2)	1.90	0.00
$Na_2[Ru(NO_2)_4(NO)(OH)] \cdot 2H_2O$[d]	NO^+	OH^-	1.950 (5)	1.99	−0.04
$Ru(NO)(S_2CN(C_2H_5)_2)_3$[e]	NO^+	$-S_2CN(C_2H_5)_2$	2.40 (1)	2.40	0.00
$[CoCl(NO)(en)_2][ClO_4]$[f]	NO^-	Cl	2.576 (3)	2.26	0.31
$[Co(NH_3)_5NO]Cl_2$[g]	NO^-(?)[h]	NH_3	2.29	1.96	0.33

Other Complexes

Complex	Ligand (L)	Trans ligand (X)[i]	M–L, Å	M–X, Å	Expected M–X, Å	Trans influence lengthening, Å
$[Co(NH_3)_5Cl][SiF_6]$[j]	Cl^-	NH_3	2.303 (6)	2.01 (2)	2.00	0.01
$[Co(NH_3)_5NO_2]Br_2$[k]	NO_2^-	NH_3	1.92 (2)	2.00 (2)	1.98	0.02
$Co(en)_2SO_3(NCS)$[l]	SO_3^{2-}	$-NCS^-$	2.203 (6)	1.974 (18)	1.97	0.00
$[Co(CH_3)(H_2O)L_4](ClO_4)$[m]	CH_3	H_2O	1.99 (4)	2.14 (2)	1.88	0.28
$Co(C_2H_3)(H_2O)(acen)$[n]	$C_2H_3^-$	H_2O	1.89 (1)	2.221 (7)	1.92	0.30
$[Ru(NH_3)_4Cl(SO_2)]Cl$[o]	SO_2	Cl^-	2.072 (3)	2.415 (3)	2.42	0.00
$[Rh(NH_3)_5(C_2H_5)]Br_2$[p]	$C_2H_5^-$	NH_3	2.048 (16)	2.256 (8)	2.07	0.19

[a] The numbers in parentheses are esd's in the last figure quoted. [b] In all but two instances, the expected M–X distances are obtained "internally." The covalent radius of the metal is calculated by using cis metal–ligand distances within the molecule which are not influenced by multiple bonding. The two exceptions are compound two listed under nitrosyls, Ru(II) = 1.33 Å, and compound five under other complexes, Co(III) = 1.22 Å. [c] Reference 18. [d] Reference 19. [e] Reference 23. [f] This work. [g] D. A. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965); D. Dale and D. C. Hodgkiss, *ibid.*, 1364 (1965). [h] Crystals of this compound are twinned and the linear Co–N–O angle determined is probably incorrect. However, there is very good agreement between the two independent structural determinations for the Co–NH_3 distances. Other physical measurements suggest that this is formally a complex of Co(III) and NO^-. [i] In the L–N–X group, X has the smallest value of the metal ($p\sigma$)–ligand hybrid (σ) overlap integral as calculated in ref 28. [j] J. A. Stanko and I. C. Paul, *Inorg. Chem.*, **6**, 486 (1967). [k] F. A. Cotton and W. T. Edwards, *Acta Crystallogr., Sect. B*, **24**, 474 (1968). [l] Reference 21. A recent redetermination of this structure established that this is formally a complex of NO^- with a Co–N–O angle of approximately 120°. See the abstracts for the summer meeting of the American Crystallographic Association, Aug 16–22, 1970, Ottawa, Canada. [m] S. Brückner, M. Culligaris, G. Narden, and L. Randaccio, *Inorg. Chim. Acta*, **3**, 278 (1969). L_4 is the tetradentate ligand bis(diacetyl monoxime imino)propane-1,3. [n] S. Brückner, M. Culligaris, G. Narden, and L. Randaccio, *ibid.*, **2**, 415 (1968). acen is the tetradentate ligand bis(acetylacetoneethylenediimine). [o] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965). [p] A. C. Skapsi and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).

Under this formalism, the NO^- group with an sp^2-hybridized N atom donates a lone pair of electrons to the Co atom and simultaneously acts as a moderately good π-acceptor ligand. After correction for thermal vibration, in which the oxygen atom was assumed to ride on the nitrogen atom, the N–O bond distance is 1.109 (17) Å. This is at the lower end of the range of approximately 1.10–1.25 Å previously determined for nitrosyls. However, no discernible correlation between N–O length and mode of coordination is evident from current X-ray structural data on nitric oxide complexes. Unfortunately, these two atoms are particularly susceptible[11,25,26] to static disorder or large thermal vibrations in a crystal which makes an accurate determination of the N–O length difficult. Also, the N–O bond order is high—between 2 and 3—for bonded NO^- or NO^+ and the N–O distance may be relatively insensitive to bonding changes in this region.

The remarkably long Co(III)–Cl bond distance of 2.576 (3) Å indicates that the NO^- group exerts a strong structural trans influence[27] on the Cl atom in this complex. Recent calculations[28] of metal ($p\sigma$)–ligand hybrid (σ) overlap integrals for a large number of ligands and metal ions suggest that a ligand will exhibit a trans-bond weakening effect if it is a strong σ donor. π-Bonding effects were not included in these calculations, but current X-ray bond length data indicate that a weak π-acceptor ligand will lengthen a trans bond.[28] Good π-acceptor ligands such as CO and C_2H_4 do not appear to weaken trans bonds but produce a large kinetic trans effect through stabilization of the transition state. Table V gives data on the trans influence for nitric oxide complexes and, for comparison, some other six-coordinate d^6 complexes. Apparently, NO^+ has no influence on trans bonds while NO^- highly weakens them. This is consistent with the idea that NO^- is a stronger σ-donor and a weaker π-acceptor ligand than NO^+. Moreover, inspection of the table shows that NO^- in *trans*-$CoCl(NO)(en)_2^+$ exhibits a trans influence as strong as alkyl or alkenyl groups in similar six-coordinate Co(III) complexes.

In K_2OsNCl_5 the lengthening[29] of the Os–Cl bond trans to the nitrido nitrogen atom was attributed to nonbonding interactions between this atom and the cis chlorine atoms. We do not feel that this is a substantial effect in the long Co–Cl bond observed here since the average N···Cl nonbonded distance in *trans*-$CoCl(NO)(en)_2^+$ is 3.16 (1) Å while it is 3.00 (1) Å in K_2OsNCl_5. The *cis*-$CoI(NO)(en)_2^+$ ion is currently

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(25) M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967).

(26) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(27) For a recent discussion of cis and trans effects in cobalt(III) complexes see J. M. Pratt and R. G. Thorp, *Advan. Inorg. Chem. Radiochem.*, **12**, 375 (1970).

(28) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969).

(29) D. Bright and J. A. Ibers, *Inorg. Chem.*, **8**, 709 (1969).

being investigated to obtain further information on the structural trans influence of the NO^- ligand.

The two ethylenediamine rings assume an approximate symmetric gauche configuration. This conformation is commonly observed[30] in complexes containing this ligand which have no large intramolecular steric interactions between ligands or other distorting factors such as extensive hydrogen bonding. The torsion angle about the C(1)–C(2) bond is 48.5° and that about the C(3)–C(4) bond is 49.3°. The carbon atoms are approximately symmetrically disposed above and below the planes defined respectively by the atoms Co–N(1)–N(2) and Co–N(3)–N(4): C(1), −0.38 Å; C(2), 0.27 Å; and C(3), −0.28 Å; C(4), 0.38 Å. Intra- and interchelate angles average 85.3 (3) and 94.4 (3)°, respectively, which are typical values for a trans complex with two ethylenediamine ligands. Examples include *trans*-$Co(en)_2SO_3(NCS)$,[21] 86.4 (5) and 93.7°, and $[Co(en)_2](SCN)_2$,[30] 85 and 95°. The N···N distances around the rectangle formed by the four nitrogen atoms are also representative for this type of complex. An average distance of 1.50 (1) Å was determined for the C–C bonds which is in accord with that determined in other complexes containing this ligand, *e.g.*,[31] $Cr(en)_3{}^{3+}$, 1.502 (5) Å. The C–N bond lengths average 1.48 (1) Å which agrees with the value of 1.479 (5) Å accepted for the normal paraffin–quaternary amine bond.

The ClO_4^- ion displays the expected[32] geometry. If a riding model is assumed for thermal vibrations in this group, the corrected average Cl–O distance is 1.446 (7) Å.

The two ions in the crystal are partially held together by hydrogen bonding involving the perchlorate oxygen atoms and the hydrogen atoms of the ethylenediamine rings. These hydrogen bonds are summarized in Table VI. It is interesting to note that the O(4) atom of the ClO_4^- group which has the largest degree of thermal motion is not involved in the hydrogen-bonding network. Bond angles around the hydrogen atoms average 149° which is characteristic[33] of the N–H···O interaction.

TABLE VI

POSSIBLE N–H···O HYDROGEN BONDS[a]

Group	N···O, Å	O···H, Å	N–H, Å	Angle at H, deg
N(2)–H(1)N(2)[b]···O(1)[c]	3.05 (2)	2.27 (11)	0.87 (11)	149 (9)
N(2)–H(2)N(2)···O(2)	3.16 (1)	2.48 (12)	0.80 (12)	144 (10)
N(4)–H(1)N(4)···O(2)[c]	3.01 (1)	2.18 (12)	0.95 (12)	145 (10)
N(1)–H(2)N(3)···O(3)	3.12 (1)	2.50 (11)	0.89 (11)	127 (8)
N(4)–H(2)N(5)···O(3)[c]	3.10 (1)	2.32 (12)	0.78 (12)	173 (12)
N(1)–H(2)N(1)···O(4)	3.19 (1)	2.47 (11)	0.89 (11)	139 (9)

[a] Standard deviations of least significant figures are given in parentheses. [b] H(1)N(2) designates the first hydrogen atom bonded to the N(2) atom. [c] These groups have O···H distances less than 2.4 Å. This has been used as a criterion[d] to indicate an appreciable hydrogen-bonding interaction of the type N–H···O. [d] P. Jönsson and W. C. Hamilton, *Acta Crystallogr.*, *Sect. B*, **26**, 536 (1970).

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