

The Crystal Structure of (-)₅₈₉-*trans*-Dinitro-(L-3,8-dimethyltriethylenetetramine)-cobalt(III) Perchlorate, *trans*-[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄

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The crystal structure of *trans*-[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄ has been determined from the three-dimensional X-ray data collected by the diffractometer method. The compound forms orthorhombic crystals with $a = 12.82$, $b = 19.91$, $c = 6.52$ Å and $Z = 4$, in space group $P2_12_12_1$. The structure has been solved by the heavy-atom method and refined by least-squares methods with anisotropic temperature factors to give an R value of 0.088 for 888 observed reflexions. The perchlorate ion is disordered over two sites. The average Co-N(dimetriem) distance is 1.98 Å and the Co-N(NO₂) distance is 1.96 Å. The conformations of the three chelate rings are δ , λ , δ and the methyl groups lie in an equatorial position relative to the plane of the chelate ring. A potential energy minimization calculation for the three isomers of [Co(NO₂)₂(L-3,8-dimetriem)]⁺ was carried out. The strain energy decreases in the sequence: *cis*- $\alpha > trans > cis$ - β .

Introduction

There exist three isomers of L-3,8-dimethyltriethylenetetraminecobalt(III) complexes: *cis*- α , *cis*- β and *trans* (Yoshikawa, Saburi, Sawai & Goto, 1969). The stereochemical configurations of dimethyltriethylenetetramine ligands in the two isomers, clarified by X-ray analyses of *A-cis*- α -[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄ and *A-cis*- β -[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄ have been reported (Ito, Marumo & Saito, 1970, 1972). The crystal structure of the last member of the series, *trans*-[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄, has been determined in order to establish the stereochemical configuration of the complex cation. These three closely related complex cations with known structures are extremely suitable for a study of strain energies and relative stabilities. Considerable success in the calculation of strain energy has recently been made with appropriate force fields in organic (Williams, Strang & Schleyer, 1968; Boyd, 1968) and polymer (Scheraga, 1968) molecules, using efficient energy search and minimization techniques. Conformational analyses of coordination compounds have also been made with remarkable success (Gollogly & Hawkins, 1969; Snow, 1970; Buckingham, Maxwell, Sargeson & Freeman, 1970; Buckingham, Maxwell, Sargeson & Snow, 1970). In the present study, calculations of the conformational energy minimization were performed for the three isomers mentioned above, allowing all the independent internal coordinates to vary simultaneously.

Experimental

The specimens were kindly supplied by Professor S. Yoshikawa of this University. They are orange prismatic crystals elongated along the c axis. The crystal data are: C₈H₂₂ClCoN₆O₈, F.W. 424, orthorhombic, $a = 12.82 \pm 0.01$, $b = 19.91 \pm 0.01$, $c = 6.52 \pm 0.01$ Å,

$D_m = 1.71$ g.cm⁻³, $Z = 4$, $D_x = 1.70$ g.cm⁻³, linear absorption coefficient for Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) $\mu = 13.4$ cm⁻¹, space group $P2_12_12_1$ (No. 19).

The crystal used for X-ray work had dimensions 0.26 × 0.24 × 0.20 mm. The intensity data were collected on a Rigaku automatic four-circle diffractometer. The crystal was mounted with the b axis parallel to the ϕ axis of the diffractometer. The specimen had a fine mosaic structure and deteriorated in air. This certainly affected the accuracy of the intensity data. The ω -scan technique was employed and the detector slit was not used. The scan range was calculated from the formula: $2.0 + 2.0 \tan \theta$, the scan speed was 1° per min in ω and background counts of 10 sec were taken at both limits of the scan. A total of 1340 independent intensities were measured up to $2\theta = 45^\circ$ (for $2\theta > 45^\circ$ almost all reflexions had intensities less than the background). 888 of these had significantly non-zero intensities. The intensities were corrected for Lorentz and polarization factors, but corrections for absorption and extinction were not made.

Determination and refinement of the structure

The coordinates of the cobalt, chlorine and the six nitrogen atoms could be easily deduced from a three-dimensional Patterson function. The positions of the other lighter atoms except the hydrogen atoms and the oxygen atoms of the perchlorate ion were revealed from the three-dimensional Fourier synthesis phased by the Co, Cl and N atoms. The structure was then refined by a block-diagonal least-squares with isotropic temperature factors. Unit weight was given for all $|F_o|$'s larger than 20.0 and 0.2 for remainders. After five cycles, the R value reduced to 0.18 for all the 888 observed reflexions. Four further cycles of least-squares were calculated in an anisotropic mode, where the anisotropic temperature factors were of the form:

exp[-(β₁₁h²+β₂₂k²+β₃₃l²+2β₁₂hk+2β₁₃hl+2β₂₃kl)]. The R value improved to 0.14. However, refinement gave an unsatisfactory geometry for the perchlorate group. A three-dimensional difference Fourier synthesis revealed that there were many peaks around the chlorine atom which could be assigned to the perchlorate oxygen atoms. The maps were well explained if the perchlorate anion was assumed to be in a disordered state and to take two different orientations. To prevent

the parameter interaction of the disordered perchlorate oxygen atoms, it was decided to refine the atoms O(5) to O(8) for one orientation in one cycle keeping the other atoms O(9) to O(11) fixed and to refine O(9) to O(11) in the next cycle keeping O(5) to O(8) fixed. The molecular geometry of the perchlorate group was re-examined every second cycle. The populations for the two orientations were estimated from the Fourier synthesis. By these means the R value gradually fell and

Table 1. Observed and calculated structure factors (×10)

Table with 4 columns of header groups: (h, k, l, FO), (FC), (h, k, l, FO), (FC), (h, k, l, FO), (FC), (h, k, l, FO), (FC), (h, k, l, FO), (FC), (h, k, l, FO), (FC). Rows contain numerical data for structure factors.

the shape of the perchlorate group became much more reasonable. Finally the R value became 0.088, which is satisfactory in view of the rather poor data from deteriorating crystals with disordered structure. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The observed and calculated structure factors are listed in Table 1. Final atomic parameters are given in Table 2.

Results and discussion

Fig. 1 shows the arrangement of the complex ions in the unit cell viewed along the c axis. Oxygen atoms of the perchlorate ions are disordered over two sites and those shown by broken lines have a smaller population factor of 0.2. Dashed lines indicate some close intermolecular contacts. The cations and anions form chains running approximately parallel to the a and b axes, forming a two-dimensional network parallel to the plane (001).

A perspective drawing of the complex cation is presented in Fig. 2. It represents correctly the absolute configuration of the complex ion. The absolute structure of the crystal could be deduced, since the absolute configuration of the asymmetric carbon atom was known. The bond lengths and angles within the complex cation are listed in Table 3. The conformations of the two chelate rings with methyl groups are δ and that of the other ring is λ , and the methyl groups lie in equatorial positions with respect to the plane of the

chelate rings. Consequently the absolute configurations of the two asymmetric nitrogen atoms are both R .

The average distance of the Co-N(dimetriene) is 1.98 Å in agreement with the values obtained for other triene complexes (Freeman & Maxwell, 1969; Dwyer & Maxwell, 1970). However, the Co-N(NO₂) distances of 1.96 Å are slightly longer than those observed in *cis-α* and *cis-β* isomers as well as in other nitro complexes such as (–)₅₈₉-*cis*-dinitrobis[(–)₅₈₉-1,2-diaminopropane]cobalt(III) chloride (Barclay, Goldschmid & Stephenson, 1970). This elongation of Co-N(NO₂) may be due to the non-bonded interaction between hydrogen atoms of the chelate rings in *trans* configuration and oxygen atoms of the nitro groups. The average C-N and C-C distances of 1.51 and 1.55 Å are similar to those observed in other triene structures. The NCoN angles of the outer chelate rings are 85°, and that of the central one is 88°. The ligand angular strain is further evidenced at the two asymmetric nitrogen atoms, N(2) and N(3), at the two asymmetric carbon atoms C(2) and C(5) and at C(3) and C(4), as shown below:

C(1)C(2)N(2) 101.1 (1.9)° C(3)C(4)N(3) 105.5 (2.2)°
C(6)C(5)N(3) 105.7 (2.2) C(2)N(2)C(3) 122.0 (1.6)
C(4)C(3)N(2) 105.0 (1.9) C(4)N(3)C(5) 120.7 (1.8).

The dihedral angles of N-C-C-N for the two side chelate rings are 52 and 53°, and that of the central chelate ring is 53°. It is interesting that the dihedral angles about the C-C bond of the chelate rings are rather small in both *cis-α* and *cis-β* forms, whereas they

Table 2. *Final positional parameters and thermal parameters and their standard deviations (in parentheses)*

The values have been multiplied by 10⁴ (except for those of m^*)
The β_{ij} values refer to the expression: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

| | x | y | z | Population m^* | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|------------|-----------|------------|---------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Co | 864 (2) | 4000 (2) | 6341 (4) | | 40 (1) | 19 (1) | 99 (5) | -4 (1) | -2 (4) | -2 (3) |
| Cl | 35 (9) | 1404 (4) | 2584 (15) | | 154 (8) | 32 (2) | 309 (20) | 4 (4) | -7 (12) | -6 (6) |
| N(1) | 2162 (15) | 3870 (11) | 4768 (29) | | 76 (16) | 34 (7) | 176 (50) | -8 (10) | 19 (24) | 11 (18) |
| N(2) | 892 (16) | 3022 (8) | 6691 (21) | | 81 (14) | 22 (5) | 52 (37) | -5 (9) | -30 (26) | -11 (11) |
| N(3) | -362 (13) | 3990 (10) | 8123 (26) | | 51 (11) | 27 (6) | 212 (54) | -7 (9) | -29 (21) | 0 (18) |
| N(4) | 603 (13) | 4995 (8) | 5942 (26) | | 57 (14) | 25 (6) | 140 (49) | -3 (7) | 4 (24) | -5 (14) |
| N(5) | 1748 (14) | 4219 (9) | 8633 (32) | | 57 (13) | 39 (8) | 157 (45) | -3 (8) | 8 (30) | 15 (18) |
| N(6) | 30 (13) | 3859 (9) | 3821 (28) | | 59 (12) | 29 (6) | 136 (42) | 2 (8) | -12 (26) | 14 (18) |
| C(1) | 2401 (19) | 3125 (11) | 4724 (34) | | 63 (18) | 25 (8) | 169 (58) | 17 (10) | -34 (32) | -6 (19) |
| C(2) | 2029 (17) | 2785 (12) | 6616 (49) | | 33 (14) | 23 (7) | 502 (107) | 0 (9) | 7 (39) | 63 (28) |
| C(3) | 153 (22) | 2822 (13) | 8442 (37) | | 100 (24) | 36 (9) | 151 (62) | -7 (13) | -17 (39) | -19 (23) |
| C(4) | -797 (24) | 3280 (10) | 8202 (34) | | 155 (28) | 13 (6) | 221 (72) | -12 (13) | 139 (45) | -2 (16) |
| C(5) | -1022 (22) | 4554 (15) | 7478 (43) | | 77 (24) | 50 (11) | 317 (78) | 28 (15) | -9 (42) | -4 (28) |
| C(6) | -273 (30) | 5166 (14) | 7264 (40) | | 189 (42) | 37 (10) | 177 (68) | 44 (17) | 95 (46) | 0 (23) |
| C(7) | 2169 (23) | 2008 (14) | 6638 (54) | | 109 (26) | 38 (10) | 387 (110) | 2 (13) | 36 (52) | 18 (32) |
| C(8) | -1906 (23) | 4725 (17) | 9097 (42) | | 103 (27) | 71 (14) | 188 (81) | 16 (17) | 32 (41) | -34 (31) |
| O(1) | 2381 (13) | 4655 (9) | 8505 (31) | | 66 (13) | 46 (7) | 375 (61) | -11 (8) | -49 (32) | 6 (22) |
| O(2) | 1652 (15) | 3953 (12) | 10312 (24) | | 116 (16) | 66 (8) | 161 (41) | 1 (13) | -63 (24) | 6 (20) |
| O(3) | -246 (24) | 4304 (9) | 2774 (31) | | 297 (37) | 39 (7) | 244 (56) | 8 (13) | -175 (39) | -22 (16) |
| O(4) | -126 (17) | 3261 (10) | 3260 (26) | | 150 (21) | 56 (8) | 197 (55) | -13 (11) | -131 (31) | -16 (16) |
| O(5) | -756 (18) | 1581 (13) | 1155 (41) | 1.0 | 141 (21) | 89 (11) | 541 (88) | 8 (15) | 74 (51) | 71 (31) |
| O(6) | 33 (53) | 722 (13) | 2801 (57) | 0.8 | 735 (104) | 27 (9) | 523 (123) | 45 (26) | -199 (101) | 23 (28) |
| O(7) | -39 (25) | 1682 (18) | 4683 (45) | 0.8 | 148 (30) | 95 (17) | 383 (96) | -26 (20) | -4 (49) | -44 (34) |
| O(8) | 974 (25) | 1715 (20) | 1948 (49) | 0.8 | 101 (26) | 137 (22) | 540 (126) | 3 (23) | -13 (57) | 14 (44) |
| O(9) | -87 (29) | 2000 (13) | 3780 (43) | 0.2 | 140 (89) | 45 (31) | 171 (213) | -45 (45) | -156 (137) | -15 (78) |
| O(10) | -510 (28) | 890 (16) | 3570 (46) | 0.2 | 152 (111) | 63 (45) | 579 (429) | 0 (63) | 0 (222) | 0 (150) |
| O(11) | 781 (22) | 1107 (14) | 1357 (46) | 0.2 | 37 (44) | 23 (21) | 676 (338) | 44 (28) | 323 (128) | -163 (79) |

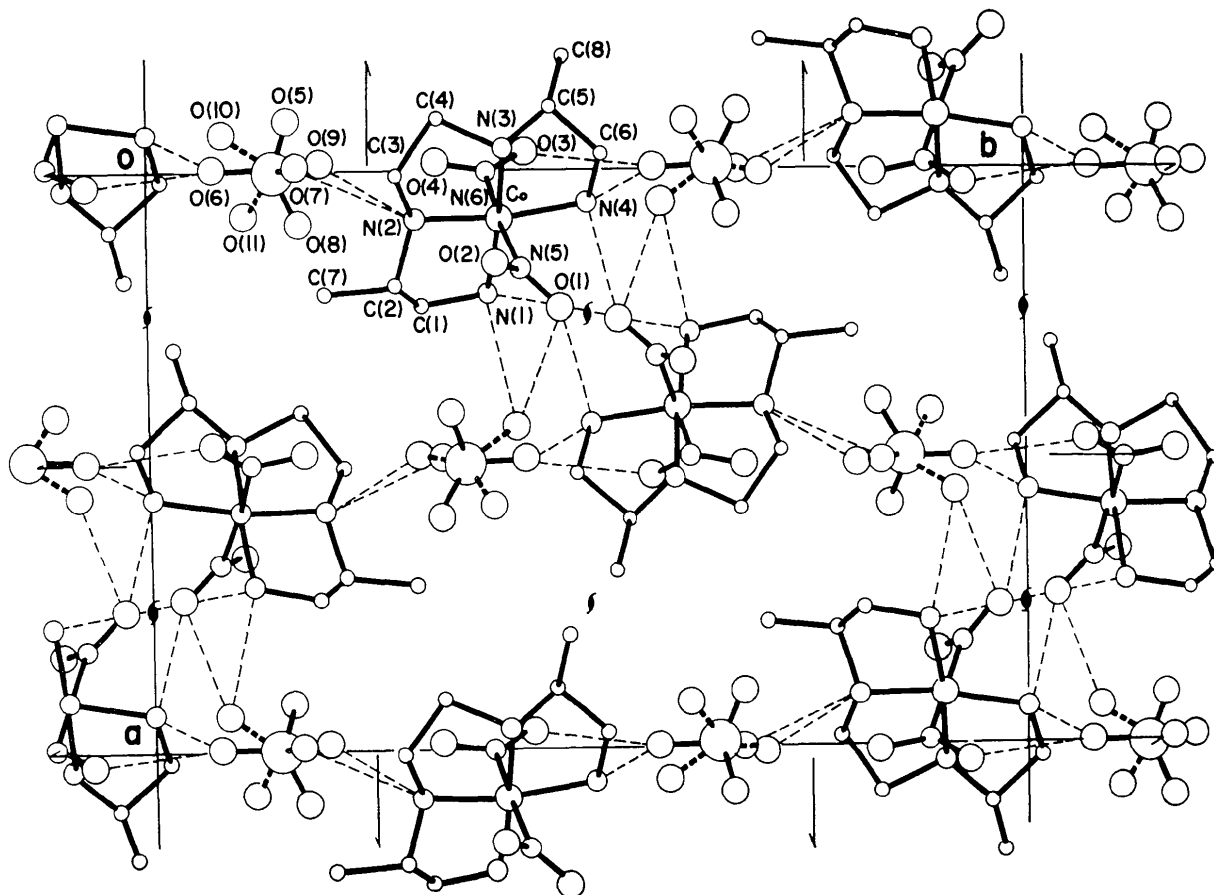


Fig. 1. Projection of the structure along the *c* axis.

are large in the *trans* isomer which has a typical *gauche* structure. The two outer chelate rings have unsymmetrical envelope conformation. The ring carbon atoms C(1) and C(2) lie at -0.02 and 0.69 Å respectively from the plane formed by N(1), Co and N(2). The corresponding deviations of C(5) and C(6) from the plane of N(3), Co and N(4) are -0.60 and 0.10 Å. In the central chelate ring, C(3) and C(4) lie 0.31 Å above and 0.44 Å respectively below the plane of N(2), Co and N(3). The *trans*-3,8-dimetricien complex as well as the *cis-α* isomer has an approximate twofold axis through the cobalt atom, bisecting the C(3)–C(4) bond. Close contacts between the coordinated nitrogen atoms and perchlorate oxygen atoms and other contacts less than 3.5 Å are listed in Table 4. They are similar to those observed in the other two isomers.

Conformational analysis

The strain energies of the three isomers were calculated according to Boyd's (1968) procedure. The strain energy, *U*, may be thought of as a sum of the following four terms: the potential energy for bond length distortion, the potential energy for bond angle distortion, the torsional potential energy of rotation about a bond and finally the non-bonded potential energy. Small defor-

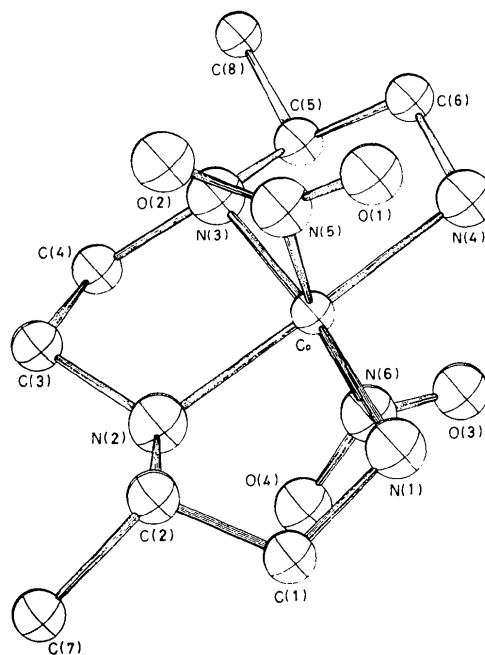


Fig. 2. A perspective drawing of the complex cation.

Table 3. *Interatomic distances and bond angles within the molecule and their estimated standard deviations (in parentheses)*

| Complex cation | | | |
|-----------------|--------------|--------------|--------------|
| Co...N(1) | 1.97 (2) Å | C(1)...N(1) | 1.51 (3) Å |
| Co...N(2) | 1.96 (2) | C(2)...N(2) | 1.53 (3) |
| Co...N(3) | 1.95 (2) | C(3)...N(2) | 1.54 (3) |
| Co...N(4) | 2.03 (2) | C(4)...N(3) | 1.52 (3) |
| Co...N(5) | 1.93 (2) | C(5)...N(3) | 1.47 (4) |
| Co...N(6) | 1.98 (2) | C(6)...N(4) | 1.46 (4) |
| | | | |
| C(1)...C(2) | 1.49 (4) | N(5)...O(1) | 1.19 (3) |
| C(3)...C(4) | 1.53 (4) | N(5)...O(2) | 1.22 (3) |
| C(5)...C(6) | 1.56 (4) | N(6)...O(3) | 1.17 (3) |
| C(2)...C(7) | 1.56 (4) | N(6)...O(4) | 1.26 (3) |
| C(5)...C(8) | 1.59 (4) | | |
| | | | |
| N(1)CoN(2) | 85.1 (0.6)° | N(1)C(1)C(2) | 111.4 (1.7)° |
| N(2)CoN(3) | 86.3 (0.5) | C(1)C(2)N(2) | 101.0 (1.7) |
| N(3)CoN(4) | 87.3 (0.5) | C(1)C(2)C(7) | 115.0 (2.3) |
| | | | |
| CoN(1)C(1) | 108.0 (0.9) | N(2)C(3)C(4) | 105.0 (1.9) |
| CoN(2)C(2) | 108.6 (1.1) | C(3)C(4)N(3) | 105.5 (2.2) |
| CoN(2)C(3) | 109.4 (0.1) | N(3)C(5)C(6) | 105.7 (2.2) |
| CoN(3)C(4) | 108.9 (0.8) | C(5)C(6)N(4) | 110.2 (2.1) |
| CoN(3)C(5) | 106.6 (1.1) | N(3)C(5)C(8) | 112.7 (2.2) |
| CoN(4)C(6) | 106.3 (1.4) | C(8)C(5)C(6) | 109.3 (2.4) |
| | | | |
| CoN(5)O(1) | 120.8 (1.5) | C(2)N(2)C(3) | 122.0 (1.6) |
| CoN(5)O(2) | 122.5 (1.2) | C(4)N(3)C(5) | 120.7 (1.8) |
| O(1)N(5)O(2) | 116.6 (1.8) | CoN(6)O(3) | 122.7 (1.6) |
| | | | |
| Perchlorate ion | | | |
| Cl...O(5) | 1.42 (3) Å | Cl...O(5) | 1.42 (3) Å |
| Cl...O(6) | 1.37 (3) | Cl...O(9) | 1.43 (3) |
| Cl...O(7) | 1.48 (3) | Cl...O(10) | 1.35 (3) |
| Cl...O(8) | 1.42 (4) | Cl...O(11) | 1.39 (3) |
| | | | |
| O(5)ClO(6) | 108.2 (1.6)° | O(5)ClO(9) | 94.2 (1.6)° |
| O(5)ClO(7) | 117.9 (1.7) | O(5)ClO(10) | 95.9 (1.8) |
| O(5)ClO(8) | 107.8 (1.8) | O(5)ClO(11) | 104.3 (1.7) |
| O(6)ClO(7) | 106.0 (1.7) | O(9)ClO(10) | 110.5 (1.9) |
| O(6)ClO(8) | 117.9 (1.9) | O(9)ClO(11) | 138.1 (1.8) |
| O(7)ClO(8) | 99.4 (1.9) | O(10)ClO(11) | 104.6 (1.9) |

mations in bond lengths and angles are assumed to be subject to harmonic restoring forces, and, therefore the adopted potential functions are of the forms: $\frac{1}{2}k_r(\Delta r)$ and $\frac{1}{2}k_\theta(\Delta\theta)$. For torsional strain the function $U_0/2(1 + \cos 3\phi)$ is used, where U_0 is the part of the experimental barrier not accounted for in non-bonding interaction part. The non-bonded interaction functions used for the calculation are Buckingham-like potentials. The stretching and bending force constants k_r and k_θ , the torsional barriers, U_0 , and the constants for non-bonding potential functions are listed in Table 5. The calculations for the minimization of U by a least-squares method were carried out by employing the program written by Dr Boyd and slightly modified by one of the authors (M.I.). The initial coordinates of the atoms were derived from the parameters of the crystal structure analysis during the refinement. The iteration was terminated and the molecular geometry calculated from the final set of coordinates when the parameter shifts were less than 0.01 Å. The torsional energy was in-

cluded only for rotation about the ligand skeleton bonds. Since unreasonably large parameter shifts arose when the starting coordinates were distant from the minimized coordinates, a very small damping factor of 0.1 was used at the initial stage and was increased as the refinement progressed.

Table 4. *Intermolecular distances less than 3.5 Å*

| Atom (1) | Atom (2) | Distances | Symmetry operation applied to second atom |
|----------|----------|-----------|---|
| N(2) | O(9) | 3.05 (3) | (1) |
| N(2) | O(7) | 3.20 (4) | (1) |
| C(3) | O(7) | 3.35 (4) | (1) |
| C(3) | O(9) | 3.46 (4) | (1) |
| C(7) | O(7) | 3.17 (4) | (1) |
| C(7) | O(8) | 3.47 (5) | (1) |
| C(7) | O(9) | 3.44 (5) | (1) |
| O(4) | O(7) | 3.28 (4) | (1) |
| O(4) | O(8) | 3.49 (4) | (1) |
| O(4) | O(9) | 2.53 (3) | (1) |
| | | | |
| N(4) | O(5) | 3.45 (3) | (2) |
| N(4) | O(6) | 2.95 (4) | (2) |
| N(4) | O(10) | 3.37 (4) | (2) |
| N(4) | O(11) | 3.23 (3) | (2) |
| C(6) | O(11) | 3.10 (4) | (2) |
| O(3) | O(6) | 2.86 (3) | (2) |
| O(3) | O(10) | 3.39 (4) | (2) |
| | | | |
| N(1) | O(10) | 3.26 (4) | (3) |
| C(1) | O(7) | 3.33 (4) | (3) |
| C(1) | O(9) | 3.37 (4) | (3) |
| C(2) | O(5) | 3.43 (3) | (3) |
| O(1) | O(5) | 3.44 (3) | (3) |
| O(1) | O(10) | 3.20 (4) | (3) |
| O(11) | C(8) | 3.38 (4) | (3) |
| | | | |
| C(6) | O(6) | 3.42 (5) | (4) |
| C(6) | O(10) | 3.30 (4) | (4) |
| | | | |
| O(1) | N(1) | 3.11 (3) | (5) |
| O(1) | N(4) | 3.11 (2) | (5) |

Key to symmetry operation

- (1) x, y, z
- (2) $-x, 0.5+y, 0.5-z$
- (3) $0.5+x, 0.5-y, 1.0-z$
- (4) $-x, 0.5+y, 1.5-z$
- (5) $0.5-x, 1.0-y, 0.5+z$

The bond lengths and angles in the complexes were reproduced within twice the standard deviations of the values obtained by structure analysis, as shown in Table 6. The major angular distortions observed in the crystals were accurately predicted from the minimization calculations. For example, a remarkable angular strain was found in the *trans* isomer at the secondary nitrogen atoms and the asymmetric carbon atoms. The final energy terms obtained from the minimization for each isomer are presented in Table 7. The calculation indicated that each isomer has different prominent energy term. Of the total strain energy, torsional strain and non-bonded interaction terms are most effective for the *cis- α* isomer, and for the *cis- β* and *trans* isomers, terms for torsional strain and bond angle deformation

are most prominent. The relative energy differences between the *cis*- α and *cis*- β isomers and between the *trans* and *cis*- β isomers are 1.2 kcal/mol and 1.7 kcal/mol

Table 5. Various constants in the potential energy functions

| Bond-stretching force constants. | | |
|----------------------------------|------------------------------------|----------------------------------|
| Bond type | k_r (millidyne.Å ⁻¹) | Strain free bond length (Å) |
| Co-N | 1.3 | 1.97 |
| N-C | 3.3 | 1.49 |
| N-O | 4.2 | 1.23 |
| N-H | 3.3 | 1.00 |
| C-C | 2.65 | 1.51 |
| C-H | 3.0 | 1.05 |
| Angle-bending force constants | | |
| Bond angle type | k_θ | Strain free bond angle (radians) |
| N-Co-N | 0.35 | 1.5708 |
| Co-N-C | 0.15 | 1.9106 |
| Co-N-H | 0.175 | 1.9106 |
| C-N-C | 0.50 | 1.9106 |
| C-N-H | 0.40 | 1.9106 |
| Co-N-O | 0.08 | 2.0945 |
| O-N-O | 0.23 | 2.0945 |
| H-N-H | 0.38 | 1.9106 |
| C-C-H | 0.40 | 1.9106 |
| C-C-C | 0.45 | 1.9106 |
| N-C-C | 0.50 | 1.9106 |
| N-C-H | 0.40 | 1.9106 |
| H-C-H | 0.35 | 1.9106 |

Table 5 (cont.)

| Torsional force constants | | | |
|--|-----------------------------|--------------------|--|
| Bond type | U_0 (kcal/mol) | | |
| C-C | 2.48 | | |
| C-N | 1.58 | | |
| Non-bonded potential function | | | |
| $U_{ij} = a \exp(-br_{ij}) - cr_{ij}^{-6}$ | | | |
| | $a(10^{-11}\text{erg/mol})$ | $b(\text{Å}^{-1})$ | $c(10^{-11}\text{erg Å}^6/\text{mol})$ |
| H...H | 46 | 4.08 | 0.339 |
| H...N | 194 | 4.32 | 0.684 |
| N...N | 1286 | 4.55 | 1.380 |
| O...H | 194 | 4.32 | 0.684 |
| C...C | 1635 | 4.32 | 2.055 |
| C...O | 1463 | 4.44 | 1.684 |
| O...O | 1286 | 4.55 | 1.380 |
| O...N | 1286 | 4.55 | 1.380 |
| C...N | 1463 | 4.44 | 1.684 |
| C...H | 217 | 4.20 | 0.836 |

References:

Nakagawa & Shimanouchi (1966).
 Abe (1971).
 Westheimer (1956).
 Schachtschneider & Snyder (1963).
 DeCoen, Elefante, Liquori & Damiani (1967).
 Liquori, Damiani & Elefante (1968).

respectively. The result indicates that the *cis*- β form is most stable among the three isomers. This is supported by the fact that the *trans* isomer is easily isomerized to the *cis*- β form by recrystallization from water. As re-

Table 6. Comparison of bond lengths and angles calculated by energy minimization with those determined from X-ray crystal structure analysis

| | <i>cis</i> - α -[Co(NO ₂) ₂ (L-3,8-dimetrien)]ClO ₄ | | <i>cis</i> - β -[Co(NO ₂) ₂ (L-3,8-dimetrien)]ClO ₄ | | <i>trans</i> -[Co-(NO ₂) ₂ (L3,8-dimetrien)]ClO ₄ | |
|--------------|--|---------|---|---------|---|---------|
| | Minimization | Crystal | Minimization | Crystal | Minimization | Crystal |
| Co...N(1) | 1.96 Å | 1.94 Å | 1.97 Å | 1.98 Å | 1.99 Å | 1.97 Å |
| Co...N(2) | 1.97 | 1.96 | 1.99 | 1.99 | 1.99 | 1.96 |
| Co...N(3) | 1.99 | 1.96 | 1.97 | 1.94 | 1.96 | 1.95 |
| Co...N(4) | 1.99 | 1.95 | 1.99 | 1.97 | 2.01 | 2.03 |
| Co...N(5) | 1.96 | 1.90 | 1.97 | 1.94 | 1.99 | 1.93 |
| Co...N(6) | 1.94 | 1.88 | 1.97 | 1.92 | 2.01 | 1.98 |
| N(1)CoN(2) | 86° | 86° | 87° | 85° | 87° | 85° |
| N(2)CoN(3) | 87 | 88 | 87 | 87 | 86 | 86 |
| N(3)CoN(4) | 86 | 87 | 86 | 86 | 88 | 87 |
| CoN(1)C(1) | 110 | 114 | 107 | 108 | 106 | 108 |
| CoN(2)C(2) | 107 | 108 | 103 | 110 | 104 | 109 |
| CoN(2)C(3) | 111 | 110 | 108 | 109 | 110 | 110 |
| CoN(3)C(4) | 109 | 108 | 109 | 110 | 107 | 109 |
| CoN(3)C(5) | 108 | 108 | 106 | 108 | 106 | 107 |
| CoN(4)C(6) | 111 | 112 | 111 | 113 | 103 | 106 |
| N(1)C(1)C(2) | 109 | 108 | 109 | 113 | 110 | 111 |
| C(1)C(2)N(2) | 108 | 107 | 106 | 104 | 104 | 101 |
| C(1)C(2)C(7) | 111 | 114 | 110 | 109 | 109 | 115 |
| C(7)C(2)N(2) | 112 | 116 | 110 | 113 | 111 | 115 |
| N(2)C(3)C(4) | 110 | 111 | 107 | 107 | 104 | 105 |
| C(3)C(4)N(3) | 111 | 111 | 110 | 109 | 103 | 106 |
| N(3)C(5)C(6) | 108 | 107 | 109 | 110 | 102 | 106 |
| C(5)C(6)N(4) | 110 | 108 | 109 | 108 | 108 | 110 |
| N(3)C(5)C(8) | 111 | 114 | 110 | 110 | 112 | 113 |
| C(8)C(5)C(6) | 113 | 114 | 111 | 116 | 111 | 109 |
| C(2)N(2)C(3) | 112 | 115 | 117 | 118 | 119 | 122 |
| C(4)N(3)C(5) | 113 | 117 | 113 | 114 | 117 | 121 |

* The numbering scheme in the original paper has been changed in conformity with that adopted for the *cis*- α and *trans* isomers.

ported by Buckingham *et al.* (1970), the calculation indicated that angular deformations are important in deriving the relative stabilities of the complex ions. In fact, bond angles deform with a comparatively small expenditure of energy for changes as large as several degrees. Similarly, torsional distortions occur easily. These angular deformations alleviate close non-bonded interactions. At present this method seems to be the most practical procedure for relating the structure, reactivity and energy of metal complexes, and is generally successful when applied to structures which vary but little from the starting models.

Table 7. *Distribution of conformational strain energy in kilocalories per mole*

| | <i>cis-α</i> | <i>cis-β</i> | <i>trans</i> |
|---|--------------|--------------|--------------|
| Bond length deformations | 0.6 | 1.3 | 0.7 |
| Bond angle deformations | 1.4 | 2.1 | 5.8 |
| Torsional strain | 5.3 | 4.2 | 2.4 |
| Non-bonded interactions | 5.5 | 3.5 | 3.4 |
| Total conformational energy | 12.8 | 11.1 | 12.3 |
| Energy differences (Relative to <i>cis-β</i>) | 1.7 | 0.0 | 1.2 |

Computing procedure

Calculation of the Fourier synthesis and the least-squares analysis were carried out on the HITAC 5020E at the Computer Centre of this University with the programs ANSR-1, HBLS-4 and ORTEP of the UNICS system written by Dr Iwasaki, Dr Ashida and Dr Johnson, respectively. All other calculations including the potential energy minimization were computed on the FACOM 270-30 computer at this Institute.

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References

- ABE, M. (1970) Private communication.
 BARCLAY, G. A., GOLDSCHMIED, E. & STEPHENSON, N. C. (1970). *Acta Cryst.* B26, 1559.
 BOYD, R. H. (1968). *J. Chem. Phys.* 49, 2574.
 BUCKINGHAM, D. A., MAXWELL, I. E., SARGESON, A. M. & FREEMAN, H. C. (1970). *Inorg. Chem.* 9, 1921.
 BUCKINGHAM, D. A., MAXWELL, I. E., SARGESON, A. M. & SNOW, M. R. (1970). *J. Amer. Chem. Soc.* 92, 3617.
 DECOEN, J. L., ELEFANTE, G., LIQUORI, A. M. & DAMIANI, A. M. (1967). *Nature, Lond.* 216, 910.
 DWYER, M. & MAXWELL, I. E. (1969). *Inorg. Chem.* 9, 1459.
 FREEMAN, H. C. & MAXWELL, I. E. (1969). *Inorg. Chem.* 8, 1293.
 GOLLOGLY, J. R. & HAWKINS, C. J. (1969). *Inorg. Chem.* 8, 1168.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 ITO, M., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* B26, 1408.
 ITO, M., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* B28, 457.
 LIQUORI, A. M., DAMIANI, A. & ELEFANTE, G. (1968). *J. Mol. Biol.* 33, 439.
 NAKAGAWA, I. & SHIMANOUCI, T. (1966). *Spectrochim. Acta*, 22, 1707.
 SCHACHTSCHNEIDER, J. H. & SNYDER, R. G. (1963). *Spectrochim. Acta*, 19, 117.
 SCHERAGA, H. A. (1968). *Advanc. Phys. Org. Chem.* 6, 103.
 SNOW, M. R. (1970). *J. Amer. Chem. Soc.* 92, 3610.
 WESTHEIMER, F. H. (1956). *Steric Effects in Organic Chemistry*, edited by NEWMAN, M. S., Chap. 12. New York: John Wiley.
 WILLIAMS, J. E., STRANG, P. J. & SCHLEYER, P. VON R. (1968). *Ann. Rev. Phys. Chem.* 19, 531.
 YOSHIKAWA, S., SABURI, M., SAWAI, T. & GOTO, M. (1969). *Proc. XII ICC, p. 155. Sydney.*