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# The Crystal Structure of Dichloro-2,2′-(1,3-diiminopropane)bis-(3-butanone oximato)cobalt(III), $[Co(C_{11}H_{19}N_4O_2)Cl_2]$

MATTI NÄSÄKKÄLÄ, HEIKKI SAARINEN, JORMA KORVENRANTA and ELINA NÄSÄKKÄLÄ

Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The title compound crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$ and with unit cell dimensions $a=9.900(6)$, $b=13.812(17)$, $c=11.702(10)$ Å, $\beta=95.47(6)°$. The structure was solved by direct methods with the MULTAN program and refined by full-matrix least-squares technique to an $R$ value of 0.043 for 1754 observed reflections. The cobalt(III) in the structure is octahedrally coordinated by the four nitrogens of the tetradentate ligand in a square plane and two chloro groups in *trans* positions. The average Co – N(oxime), Co – N(imine) and Co – Cl distances are 1.901(6), 1.927(5) and 2.251(2) Å, respectively. The O···O distance for the intramolecular hydrogen bond formed between the oxime groups is 2.453(8) Å.

The present tetradentate imine-oxime ligand, referred to as $H_2L$ in the following, results from the condensation of 1 mol of 1,3-propanediamine with 2 mol of 2,3-butanedione monoxime. Earlier studies on its metal complexes concern the structures $[Ni(HL)]ClO_4$,[1] $[Cu(HL)(CH_3OH)_{\frac{1}{2}}]ClO_4$[2] and $[CH_3Co(HL)(H_2O)]ClO_4$[3] which all contain a nearly planar arrangement of the four nitrogen donor atoms of $HL^-$ and an intramolecular O···O hydrogen bridge between the oxime oxygens. The intramolecular hydrogen bridges of the Ni(II) and Co(III) complexes are among the shortest known in the literature. Our present study of $[Co(HL)Cl_2]$ was undertaken to find out if there are any marked deviations in the geometry of the oxime groups and in the hydrogen bond length due to the different coordination environment. Cobalt complexes of this type are of special interest because their chemistry is in many ways similar to that of the cobaloximes which are widely used as model compounds for the vitamin $B_{12}$.[4]

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## EXPERIMENTAL

*Crystal preparation.* The ligand, 2,2′-(1,3-diiminepropane)bis(3-butanone oxime) $[=H_2L]$ was prepared by condensing 1 mol of 1,3-propanediamine with 2 mol of 2,3-butanedione monoxime in boiling diisopropyl ether.[5] The cobalt(III) complex was obtained by treating $H_2L$ (2.4 g, 10 mmol) in acetone with $CoCl_2.6H_2O$ (2.4 g, 10 mmol) dissolved in the minimum amount of water. After standing two days in air the precipitate that formed was leached with water and the insoluble grey-green residue (~500 mg) was dissolved in a warm acetone-ethanol mixture (1:1) from which needle-like crystals were slowly formed on cooling. The product appeared to be grey-green or red-brown in colour depending on the crystal size and the direction of the light source.

*Crystal and intensity data.* Preliminary Weissenberg photographs showed the crystals to be monoclinic. The space group was $P2_1/n$. A crystal with approximate dimensions $0.45\times0.10\times0.15$ mm was mounted on a Syntex $P2_1$ diffractometer and precise cell parameters were determined by a least-squares refinement of 13 automatically centered reflections. The crystal data for $[Co(C_{11}H_{19}N_4O_2)Cl_2]$ are: $a=9.900(6)$, $b=13.812(17)$, $c=11.702(10)$ Å, $\beta=95.47(6)°$, $Z=4$, space group $P2/_1/n$, $D_x=1.539$ g cm$^{-3}$, $D_m=1.55$ g cm$^{-3}$ (by flotation), $V=1592.8$ Å$^3$, $\mu=14.6$ cm$^{-1}$ (Mo$K\alpha$), $\lambda$(Mo$K\alpha$)$=0.7107$ Å.

X-Ray intensities were measured by the $\omega$-scan technique ($3°<2\theta<55°$) with graphite monochromatized Mo$K\alpha$ radiation. The scan rate varied from 2 to 20° min$^{-1}$, depending on the intensity of the reflection. The intensity of a test reflection remeasured after every 40 reflections showed no significant change during the data collection. Of the 3590 recorded reflections, 1754 with $I>3\sigma(I)$ were used in the calculations. The intensities were corrected for Lorentz and polarization effects.

*Structure determination and refinement.* The structure was solved by the direct methods with the MULTAN program.[6] The cobalt atom, one of the nitrogen atoms and the two chlorine atoms were located in the initial $E$ map and subsequent Fourier syntheses gave the positions of the other non-hydrogen atoms. The positional and anisotropic temperature parameters for the non-hydrogen atoms were refined by block-diagonal least-squares technique (X-RAY SYSTEM).[7] All hydrogen atoms were located on a difference Fourier map. The refinement was then continued with the hydrogen atoms isotropic. The function to be minimized was $w=(|F_o|-|F_c|)^2$, where $w=1/(20.0+|F_o|+0.02|F_o|^2)$. The final $R$ value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0.043 for 1754 observed reflections; the average shift/e.s.d. value of variable parameters was 0.18.

The atomic scattering factors for the non-hydrogen atoms were those of Cromer and Mann[8] and for the hydrogen atoms those of Stewart, Davidson and Simpson.[9] The anomalous dispersion corrections ($\Delta f'$, $\Delta f''$) were included for Co and Cl.[10]

Atomic parameters for the non-hydrogen and hydrogen atoms are listed in Tables 1 and 2, respectively. The calculated C–H bond distances are also included in Table 2.

A list of the observed and calculated structure factors is obtainable from the authors.

*Table 1.* Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms.

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| C1 | 4171(7) | 7761(5) | 1352(6) | C11 | 3840(9) | 8580(7) | 6830(8) |
| C2 | 3684(7) | 6760(5) | 1324(6) | N1 | 4298(5) | 8127(4) | 2392(5) |
| C3 | 2989(9) | 5404(5) | 2472(7) | N2 | 3495(5) | 6397(4) | 2317(5) |
| C4 | 3447(8) | 4985(5) | 3630(7) | N3 | 3315(5) | 6479(4) | 4811(5) |
| C5 | 2847(8) | 5476(5) | 4628(6) | N4 | 4091(6) | 8191(4) | 4803(5) |
| C6 | 3377(6) | 6892(5) | 5808(5) | O1 | 4731(5) | 9024(3) | 2582(5) |
| C7 | 3784(7) | 7923(5) | 5803(6) | O2 | 4482(6) | 9114(4) | 4646(5) |
| C8 | 4474(8) | 8330(6) | 320(7) | Cl1 | 1644(2) | 7813(1) | 3264(2) |
| C9 | 3450(10) | 6238(7) | 195(7) | Cl2 | 5980(2) | 6813(1) | 3872(2) |
| C10 | 3055(8) | 6442(6) | 6896(6) | Co | 3805(1) | 7292(1) | 3574(1) |

*Table 2.* Fractional atomic coordinates ($\times 10^3$), isotropic thermal parameters ($\times 10^2$) and bond distances (Å) for the hydrogen atoms.

| Atom | *X/a* | *Y/b* | *Z/c* | *U* | Bond length |
|---|---|---|---|---|---|
| H1(C3) | 328(8) | 496(6) | 179(6) | 6(2) | 1.07(8) |
| H2(C3) | 203(8) | 545(5) | 247(7) | 6(2) | 0.95(8) |
| H1(C4) | 306(9) | 427(6) | 351(7) | 6(3) | 1.07(8) |
| H2(C4) | 442(7) | 506(5) | 367(6) | 6(2) | 0.96(7) |
| H1(C5) | 311(7) | 513(5) | 521(6) | 4(2) | 0.85(7) |
| H2(C5) | 192(6) | 540(4) | 448(5) | 3(2) | 0.93(6) |
| H1(C8) | 482(9) | 895(6) | 64(7) | 9(3) | 0.98(9) |
| H2(C8) | 508(8) | 806(6) | −16(7) | 8(3) | 0.93(8) |
| H3(C8) | 370(10) | 838(7) | −38(8) | 12(3) | 1.07(9) |
| H1(C9) | 317(10) | 663(7) | −41(8) | 11(3) | 0.92(10) |
| H2(C9) | 423(9) | 591(6) | 8(8) | 9(3) | 0.92(9) |
| H3(C9) | 287(11) | 574(7) | 16(9) | 13(4) | 0.90(11) |
| H1(C10) | 279(8) | 577(6) | 672(7) | 8(3) | 0.98(8) |
| H2(C10) | 372(10) | 640(7) | 762(8) | 11(3) | 1.02(9) |
| H3(C10) | 239(11) | 679(8) | 716(9) | 13(4) | 0.89(11) |
| H1(C11) | 456(11) | 898(8) | 715(9) | 14(4) | 0.95(11) |
| H2(C11) | 297(9) | 892(7) | 694(7) | 9(3) | 1.00(9) |
| H3(C11) | 367(13) | 819(9) | 755(10) | 20(5) | 1.03(13) |
| H(O2) | 473(10) | 916(7) | 377(8) | 11(3) | 1.08(10) |

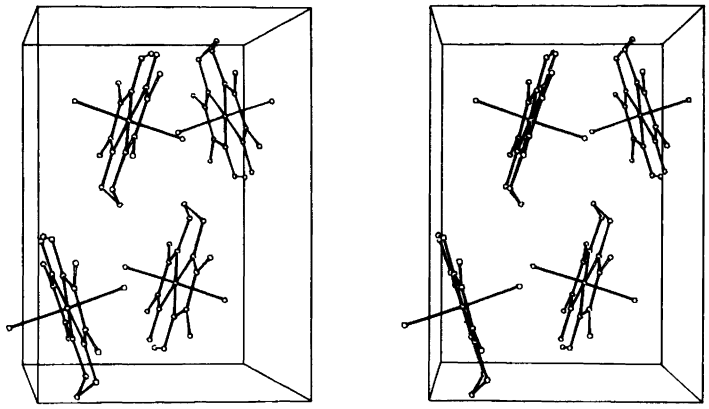

*Fig. 1.* A stereoscopic illustration of the structure.

## RESULTS AND DISCUSSION

The structure consists of discrete neutral $[Co(HL)Cl_2]$ complex molecules. The slightly distorted octahedron about cobalt(III) consists of the two oxime and two imine nitrogens from the tetradentate ligand in a square-planar arrangement and two chloro groups in *trans* positions. The crystal structure is shown in Fig. 1, the intramolecular distances are presented in Fig. 2, and the bond angles are collected in Table 3.

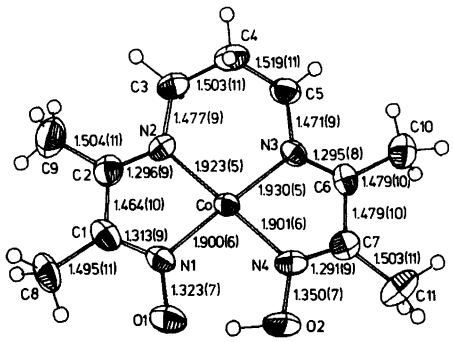


*Fig. 2.* ORTEP drawing of the molecule including bond lengths (Å). For the sake of clarity, the chloro groups in *trans* positions are not shown

Comparison of the ligand dimensions with those previously reported for the square-planar $[Ni(HL)]ClO_4$,[1] octahedral $[Cu(HL)(CH_3OH)_{\frac{1}{2}}]ClO_4$[2] and $[CH_3Co(HL)(H_2O)]ClO_4$[3] complexes of the same ligand shows no marked differences. The average N–O(oxime) [1.337(7) Å] and C=N-(oxime) [1.302(9) Å] bond lengths are also in good agreement with those observed in metal dioximates[11] and amino-oximates.[12–15]

The Co–N(oxime) distance of 1.901(6) Å is remarkably similar to this bond in several other octahedral Co(III) complexes. The average Co–N-(imine) distance of 1.927(5) Å obtained here seems to be slightly longer than the Co–N(oxime) bond, which is a trend also observed in the other Ni, Cu

*Table 3.* Interatomic angles (°).

| | | | | | |
|---|---|---|---|---|---|
| C2–C1–C8 | 124.7(6) | C10–C6–N3 | 126.5(6) | N3–Co–N4 | 80.9(2) |
| C2–C1–N1 | 112.7(6) | C6–C7–C11 | 124.6(6) | N1–Co–Cl1 | 89.7(2) |
| C8–C1–N1 | 122.6(6) | C6–C7–N4 | 111.5(6) | N1–Co–Cl2 | 89.0(2) |
| C1–C2–C9 | 119.7(7) | C11–C7–N4 | 123.9(7) | N2–Co–Cl1 | 90.1(2) |
| C1–C2–N2 | 114.9(6) | C1–N1–O1 | 121.1(6) | N2–Co–Cl2 | 90.6(2) |
| C9–C2–N2 | 125.3(7) | C2–N2–C3 | 123.3(6) | N3–Co–Cl1 | 90.2(2) |
| C4–C3–N2 | 113.0(6) | C5–N3–C6 | 122.3(6) | N3–Co–Cl2 | 91.1(2) |
| C3–C4–C5 | 114.5(6) | C7–N4–O2 | 119.3(6) | N4–Co–Cl1 | 89.1(2) |
| C4–C5–N3 | 113.1(6) | N1–Co–N2 | 82.4(2) | N4–Co–Cl2 | 90.2(2) |
| C7–C6–C10 | 119.3(6) | N2–Co–N3 | 99.6(2) | Cl1–Co–Cl2 | 178.4(1) |
| C7–C6–N3 | 114.2(6) | | | | |

*Table 4.* Deviation of atoms (Å) from CoN1N2N3N4 least squares plane.

| Atom | Dev. | Atom | Dev. |
|---|---|---|---|
| C1 | −0.046 | C11 | −0.232 |
| C2 | −0.073 | N1 | 0.004 |
| C3 | −0.039 | N2 | −0.007 |
| C4 | 0.663 | N3 | 0.004 |
| C5 | −0.016 | N4 | −0.007 |
| C6 | −0.029 | O1 | 0.040 |
| C7 | −0.091 | O2 | −0.053 |
| C8 | −0.097 | Cl1 | −2.247 |
| C9 | −0.163 | Cl2 | 2.253 |
| C10 | −0.041 | Co | 0.006 |

and Co complexes of the ligand referred to above. The two chloro groups, not included in Fig. 2, are nearly equidistant from the cobalt atom [2.254(2) and 2.247(2) Å], and the Cl−Co−Cl angle of 178.4(1)° does not deviate markedly from 180°.

Table 3 shows that the angles about the oxime and imine nitrogens deviate somewhat from 120°, with four smaller angles [114.2(5)−117.9(5)°] and eight larger angles [119.3(6)−123.3(6)°]. The smaller ones are opposite angles in the five-membered chelate rings. The deviations are evidently brought about by the steric requirements of the chelate rings. Correspondingly the angles about the $sp^2$ carbons range from 111.5(6) to 114.2(6)° and from 119.3(6) to 126.5(6)°, with the smaller angles occurring in the chelate rings. On the other hand, the angles of the $sp^3$ carbon atoms in the six-membered ring are opened from the tetrahedral value, and range between 113.0(6) and 114.5(6)°.

The four nitrogen atoms and the cobalt atom are nearly coplanar, the maximum deviation from their least-squares plane being 0.007 Å. An interesting feature of the structure is that ten of the total eleven carbon atoms lie slightly below this plane (Table 4). The one exception is the middle carbon atom of the propylene bridge which is clearly (0.663 Å) above the plane. Thus the chelate ring has the expected conformation, the torsional angles about the C3−C4 and C4−C5 bonds being 67.5° and −66.7°, respectively. The oxime oxygen atoms of the structure are slightly displaced to opposite sides (+0.040 and −0.052 Å) of the plane defined by the Co and N atoms. By contrast the oxime oxygens of the corresponding nickel complex lie closely in the $NiN_4$ plane.[1]

The intramolecular hydrogen bond between the oxime oxygen atoms is typical of complexes of this type. The O1···O2 separation of 2.453(8) Å is not much longer than the shortest accurately known O···O distances (~2.40 Å) and can be compared with that found in nickel dioximates (2.40−2.45 Å),[11] in $[Ni(HL)]ClO_4$ [2.425(8) Å],[1] in the nickel(II) and cobalt(III) complexes of bidentate 2-amino-2-methyl-3-butanone oxime [2.420(3) and 2.422(3) Å],[12,13] and in complexes of the same metal ions formed by similar tetradentate amino-oxime ligands [2.432(3)−2.474(6) Å].[14,15] The O···O distance of 2.39 Å reported for $[CH_3Co(HL)(H_2O)]ClO_4$[3] is obviously too short. This conclusion is supported by the relatively inaccurate bond lengths given and especially the fact that hydrogen atoms were not included in the refinement of the structure. In general we have found the non-inclusion of hydrogen atoms to result in too short O···O distances.

*Table 5.* Intermolecular distances (Å) below 3.7 Å between the non-hydrogen atoms.

| | | |
|---|---|---|
| O2−O2 | $(1-x,2-y,1-z)$ | 2.753(7) |
| O1−C3 | $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ | 3.295(10) |
| O1−C10 | $(\frac{1}{2}+x,\frac{3}{2}-y,-\frac{1}{2}+z)$ | 3.520(10) |
| O1−C4 | $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ | 3.581(9) |
| O1−C11 | $(1-x,2-y,1-z)$ | 3.638(10) |
| Cl1−C11 | $(-\frac{1}{2}+x,\frac{3}{2}-y,-\frac{1}{2}+z)$ | 3.652(9) |

Although the positions found in this study for the hydrogen atoms should be considered only approximate, the oxime proton appears to be 1.08(10) Å from the O2 atom and 1.40(10) Å from the O1 atom, the O2−H···O1 angle being 163(9)°. The result argues against the presence of a symmetrical hydrogen bond, often proposed in the case of such short O···O distances. In this respect the results obtained for $[Ni(HL)]ClO_4$ were closely similar.[1]

Intermolecular distances below 3.7 Å (ignoring hydrogens) are presented in Table 5. One of the distances is unusually short: the distance between the oxime oxygens O2 and O2′ $[1-x, 2-y, 1-z]$ of 2.753(7) Å is shorter than the sum of the van der Waals radii (2.80 Å)[16] and suggestive of hydrogen bonding. However, this is most improbable, as the H(O2)···O2′ distance of 3.08(10) Å is long enough to rule out any substantial hydrogen bonding. In any case, the present intramolecular hydrogen bond must be strongly influenced by the crystal packing forces around the oxime oxygen atoms.

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