  Bull. Chem. Soc. Jpn., 61, 3519—3523 (1988) 

# The X-Ray Structure of Sodium *trans*-1,2-Cyclohexanediamine-*N,N,N',N'*-tetraacetatochromate(III) 4.5-Hydrate, Na[Cr(cydta)]·4.5$H_2O$

Sumio KAIZAKI,*,† Mariko HAYASHI, Keisuke UMAKOSHI,†† and Shun-ichiro OOI††
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630
††Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558
(Received March 22, 1988)

The crystal structure of the title compound has been determined from the X-ray diffraction data. This complex crystallizes in the monoclinic space group with unit-cell parameters of $a$=17.724(2), $b$=8.084(1), $c$=14.025(2) Å, $\beta$=95.06(1)°, and $Z$=4, and with a space group of $P2/c$. The structure converged to $R$=0.043 for 2898 reflections. In the complex anion, the chromium is coordinated by the sexadentate cydta ligand, producing a distorted octahedral $CrN_2O_4$ geometry. The glycinate chelates of the in-plane G(girdling) rings in the $CrN_2O_2$ plane are more distorted with respect to the Cr-O bond lengths and internal bond angles than are those of the out-of-plane R(relaxed) rings in the $CrNO_3$ plane. This may be responsible for the lability to dissociation of the G-ring acetate chelates. A close proximity of non-bonded hydrogen atoms (ca. 1.90 Å) is found between the methylene groups in the R ring and the cyclohexane ring. There are two nonequivalent sodium ions in the unit cell, which link the cydta complex anions to form an anion layer along the c axis.

Only two X-ray structure studies have been reported for six-coordinated sexadentate *trans*-1,2-cylcohexanediamine-*N,N,N',N'*-tetraacetatometallate ([M(cydta)]$^{n-}$); Manganate(III)[1] and cupurate(II),[2] both of which are severely distorted from a regular octahedron, though in opposite direction from each other, as a result of the Jahn-Teller effect. For non Jahn-Teller distorted cydta complexes, the X-ray structure data will make it possible to understand some characteristics of the thermodynamic, kinetic, and NMR and chiroptical spectroscopic behavior, which has suggested that the G-ring chelates are more labile to dissociation than the R-ring ones and that the sexadentate coordination of the cydta ligand in metal complexes is more favorable than that of the ethylenediamine-*N,N,N',N'*-tetraacetate (edta) one.[3-10] For such a study, the cydta Cr(III) complex is appropriate, because there have been reported some X-ray structure data of edta-like Cr(III) complexes[11-15] including K[Cr(edta)]·2$H_2O$, the solution structure of which has been well investigated, though there has long remained a controversy over whether it has a sexa- or quiquedentate edta coordination.[7-10]

This paper will report the determination of the crystal and molecular structure of Na[Cr(*rac*-cydta)]·4.5$H_2O$ by means of X-ray structure analysis.

## Experimental

**X-Ray Analaysis of Na[Cr(cydta)]·4.5$H_2O$.** Violet crystals of this complex suitable for X-ray analysis were obtained by the literature method[16] and then grown from a concentrated aqueous solution in a refrigerator for a few days. The elemental analysis showed 4.5 hydrate of this complex, in accord with the crystallographic result, though Tanaka et al. reported 4 hydrate.[16] Anal Calcd for Na[Cr(cydta)]·4.5$H_2O$: C, 33.74; H, 5.46; N, 5.62%. Found: C, 33.64; H, 5.44; N, 5.62%.

† Present address: Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560.

The crystal data and experimental details are shown in Table 1. Weissenberg photography was used for the determination of the space group. The unit-cell parameters were derived by a least-squares analysis of 2$\theta$ values of the reflections in the $14<2\theta<23°$ range, measured on a Philips PW1100 diffractometer by the use of Mo$K\alpha$ radiation ($\lambda$=0.7107 Å). The intensity data were collected on the diffractometer by using graphite-monochromated Mo$K\alpha$ radiation at room temperature. The intensities of three standard reflections (600, 010, 004), monitored every 4h, showed no appreciable decay during the data collection. Of the 4814 unique reflections measured in the $h$, $k$, $\pm l$ region, 2898 with $F_o^2>3\sigma(F_o^2)$ were used for the structural analysis. No correction was made for absorption.

The crystal structure was solved by the direct method

Table 1. Crystallographic Data for Na[Cr(*rac*-cydta)]·4.5$H_2O$

| | |
|---|---|
| Formula | $C_{14}H_{27}N_2O_{12.5}NaCr$ |
| Space group | $P2/c$ |
| $a$/Å | 17.724(1) |
| $b$/Å | 8.084(1) |
| $c$/Å | 14.025(2) |
| $\beta$/deg | 95.060 |
| $V$/Å$^3$ | 2002.6(4) |
| $Z$ | 4 |
| $D_m$/g cm$^{-3}$ | 1.65 |
| $D_c$/g cm$^{-3}$ | 1.654 |
| Cryst size/mm | 0.095×0.2×0.19 |
| Cryst color | blue violet |
| Cryst faces | (001) (00$\bar{1}$) (010) (0$\bar{1}$0) (100) ($\bar{1}$00) |
| $\mu$(Mo$K\alpha$)/cm$^{-1}$ | 6.438 |
| Scan method | $\omega$ |
| Scan speed/deg s$^{-1}$ | 0.033 |
| Scan width/deg | 1.0+ 0.4 tan $\theta$ |
| Data colln range(2$\theta$)/deg | 4—46 |
| No. of observed reflections [$F_o^2>3\sigma(F_o^2)$] | 2898 |
| $R_F$[a] | 0.0430 |
| $R_{WF}$[b] | 0.0504 |

a) $R_F=\sum||F_o|-|F_c||/\sum|F_o|$.
b) $R_{WF}=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w=\sigma(|F_o|)^{-2}$.

(MULTAN).[17] The positional and thermal parameters were refined by the block-diagonal least-squares method. The minimized function was $\sum w(|F_o|-|F_c|)^2$, where $w=\sigma(F_o)^{-2}$. Hydrogen atoms were introduced in the calculated positions (C-H=0.97 Å), but those of the water molecules were located on a difference synthesis map except for one of the H atoms bonded to O(W1). These H atoms were included in the least-squares calculation, but their parameters were not refined. Each H atom was assigned an isotropic temperature factor equal to that of the atom to which it is bonded. The convergence was attained with the $R_F$ and $R_{WF}$ values listed in Table 1. All the parameter shifts in the final cycle of the refinement were $<0.2\sigma$. The final difference synthesis showed no peak greater than 0.7 e Å$^{-3}$. The atomic scattering factors, with correction for the real part of the anomalous dispersion effect for Cr and $Na^+$, were taken from Ref. 18. Tables of the observed and calculated structure factors, thermal parameters, and hydrogen-atom coordinates are deposited as Document No. 8828 at the Office of the Editor of the Bull. Chem. Soc. Jpn. The computational work was carried out by using standard programs.[19] The atomic coordinates are given in Table 2.

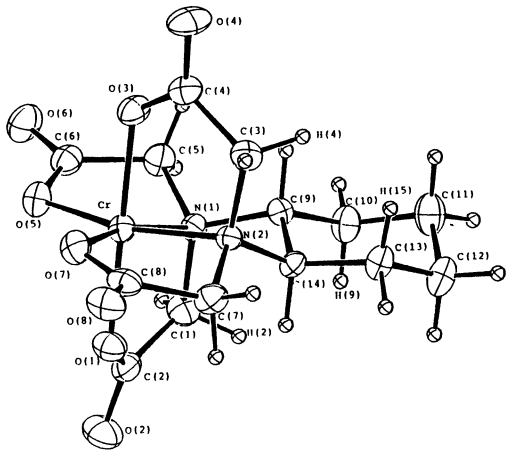


Fig. 1. The molecular structure of [Cr(cydta)]$^-$ ion in its sodium 4.5-hydrate. Thermal elipsoids are drawn at 50% probability level. Hydrogen atoms are represented as spheres of arbitrary radius. Besides Cr, C, N, and O atoms, only four hydrogen atoms which exhibit the close contact are numbered for clarity (see Text).

## Results and Discussion

**The Complex Anion [Cr(cydta)]$^-$.** A perspective drawing of [Cr(cydta)]$^-$ is shown in Figure. 1. The bond lengths and angles are summarized in Table 3. The average bond lengths and angles, together with the torsion angles, are listed in Tables 4 and 5. The crystal structure analysis confirmed the sexadentate six-coordination mode of *trans*-1,2-cyclohexanediaminetetraacetate in this chromium(III) complex, as evidenced by our recent chiroptical study[8] and as found in K[Cr(edta)]·2$H_2O$.[11] The bond lengths and angles of the edta sub-unit in [Cr(cydta)]$^-$ are almost identical with those of the edta complex. The coordination geometry of the present complex anion is a distorted octahedron, with N-Cr-O and O-Cr-O angles of 81.2 and 112.9° respectively in the $CrN_2O_2$ plane. The Cr-N bond distances (2.058 Å) are as long as those of the edta complex[11] and the 1,3-propanediaminetetraacetato chromate(III) ([Cr(1,3-pdta)]$^-$)[12] and *cis*(*N*)-bis(iminodiacetato)chromate(III)-([Cr(ida)]$^-$)[13] complexes, but are shorter than those (average 2.085 Å) of *trans*($O_5$)-(ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-dipropionato) chromate(III) ([Cr-(eddda)]$^-$)[14] and *trans*($O_6$)-(1,3-propanediamine-*N*,*N*′-diacetato-*N*,*N*′-dipropionato)chromate(III) ([Cr(1,3-pddda)]$^-$).[15] The Cr-O bonds fall into two classes with a mean bond length of 1.97 Å. The Cr-O bonds in G-ring chelates (average 1.992 Å) are longer than those (1.95—1.97 Å) usually found for the 1,3-pdta, bis(ida), and 1,3-pddda complexes,[12-15] whereas those in the R-ring chelates (average 1.953 Å) are almost the same. In other words, the differences between the Cr-O(R) and Cr-O(G) bond lengths for the edta and cydta complexes are larger than those for the bis(ida)[13] and 1,3-pdta[12] complexes, though these differences are smaller than those for the corresponding Mn(III) and Cu(II) complexes, the structures of which are susceptible to Jahn-Teller distortion[1,2] The sums of the G-ring bond angles in the cydta complex (average 524.0°) are samller than those of the R-ring ones (average 536.4°). The torsion anlges for the Cr-N-C-C chains

Table 2. Atomic Coordinates and Thermal Parameters

| Atom | *X* | *Y* | *Z* | *U*(EQ) or *U* |
|---|---|---|---|---|
| Cr | 0.30612(3) | 0.0458(1) | 0.1319(4) | 0.0163(2) |
| Na(1) | 0.5 | 0 | 0.5 | 0.028(1) |
| Na(2) | 0.5 | 0.5 | 0.5 | 0.030(1) |
| O(1) | 0.2673(1) | 0.1773(3) | 0.0215(2) | 0.025(1) |
| O(2) | 0.1680(2) | 0.1891(4) | −0.0870(2) | 0.039(2) |
| O(3) | 0.3416(1) | −0.0911(3) | 0.2414(2) | 0.028(1) |
| O(4) | 0.4062(2) | −0.0757(3) | 0.3846(2) | 0.039(2) |
| O(5) | 0.2830(1) | −0.1648(3) | 0.0607(2) | 0.025(1) |
| O(6) | 0.2139(2) | −0.3934(3) | 0.0719(2) | 0.048(2) |
| O(7) | 0.4099(1) | 0.1289(3) | 0.1177(2) | 0.018(1) |
| O(8) | 0.4805(1) | 0.3559(4) | 0.1381(2) | 0.022(1) |
| O(W1) | 0.0109(2) | −0.2262(4) | 0.3489(3) | 0.037(2) |
| O(W2) | 0.4408(2) | −0.2546(4) | 0.0590(2) | 0.036(2) |
| O(W3) | 0.3775(2) | −0.4086(4) | 0.4274(2) | 0.043(2) |
| O(W4) | 0.0595(2) | −0.5041(4) | 0.0778(2) | 0.060(2) |
| O(W5) | 0.5 | −0.3122(6) | 0.25 | 0.145(2) |
| N(1) | 0.1935(1) | 0.0226(4) | 0.1548(2) | 0.020(1) |
| N(2) | 0.3093(1) | 0.2344(4) | 0.2310(2) | 0.016(1) |
| C(1) | 0.1478(2) | 0.0897(5) | 0.0675(3) | 0.021(2) |
| C(2) | 0.1969(2) | 0.1546(5) | −0.0069(3) | 0.028(2) |
| C(3) | 0.3490(2) | 0.1698(5) | 0.3223(3) | 0.023(2) |
| C(4) | 0.3680(2) | −0.0122(5) | 0.3165(3) | 0.017(2) |
| C(5) | 0.1819(2) | −0.1596(5) | 0.1642(3) | 0.026(2) |
| C(6) | 0.2285(2) | −0.2492(5) | 0.0934(3) | 0.025(2) |
| C(7) | 0.3561(2) | 0.3644(5) | 0.1908(3) | 0.024(2) |
| C(8) | 0.4219(2) | 0.2792(5) | 0.1460(3) | 0.019(2) |
| C(9) | 0.1836(2) | 0.1193(4) | 0.2454(2) | 0.020(2) |
| C(10) | 0.1008(2) | 0.1464(5) | 0.2656(3) | 0.018(2) |
| C(11) | 0.0975(2) | 0.2573(5) | 0.3533(3) | 0.026(2) |
| C(12) | 0.1326(2) | 0.4239(5) | 0.3354(3) | 0.029(2) |
| C(13) | 0.2164(2) | 0.4026(5) | 0.3206(3) | 0.024(2) |
| C(14) | 0.2276(2) | 0.2818(4) | 0.2391(3) | 0.017(2) |

Table 3. Bond Distances and Bond Angles around the Complex Anion and Cation

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Bond distance/Å | | | | | | | |
| Cr-O(1) | 1.954(3) | O(8)-C(8) | 1.224(4) | O(4)-C(4) | 1.233(4) | C(5)-C(6) | 1.528(5) |
| Cr-O(3) | 1.951(3) | N(1)-C(1) | 1.508(4) | O(5)-C(6) | 1.299(4) | C(7)-C(8) | 1.535(5) |
| Cr-O(5) | 1.998(3) | N(1)-C(5) | 1.495(5) | O(6)-C(6) | 1.290(5) | C(9)-C(14) | 1.534(5) |
| Cr-O(7) | 1.985(2) | N(1)-C(9) | 1.515(5) | C(8)-O(7) | 1.290(5) | C(10)-C(11) | 1.527(6) |
| Cr-N(1) | 2.058(3) | N(2)-C(3) | 1.499(4) | C(9)-C(10) | 1.534(5) | C(12)-C(13) | 1.527(5) |
| Cr-N(2) | 2.060(3) | N(2)-C(7) | 1.481(5) | C(11)-C(12) | 1.514(6) | C(13)-C(14) | 1.529(5) |
| O(1)-C(2) | 1.289(4) | N(2)-C(14) | 1.512(4) | Na(1)-O(7)[a] | 2.617(3) | Na(1)-O(4) | 2.298(3) |
| O(2)-C(2) | 1.226(4) | C(1)-C(2) | 1.511(5) | Na(1)-O(W2)[a] | 2.485(3) | Na(2)-O(8)[a] | 2.312(3) |
| O(3)-C(4) | 1.284(4) | C(3)-C(4) | 1.514(5) | Na(2)-O(W3)[b] | 2.430(3) | Na(2)-O(W2)[c] | 2.424(3) |
| Bond angle/deg | | | | | | | |
| O(1)-Cr-O(3) | 177.9(1) | Cr-O(1)-C(2) | 115.5(2) | C(3)-N(2)-C(14) | 113.9(3) | N(2)-C(7)-C(8) | 108.0(3) |
| O(1)-Cr-O(5) | 91.4(1) | Cr-O(3)-C(4) | 115.6(2) | C(7)-N(2)-C(14) | 113.9(3) | O(7)-C(8)-O(8) | 124.5(3) |
| O(1)-Cr-O(7) | 90.0(1) | Cr-O(5)-C(6) | 113.4(2) | N(1)-C(1)-C(2) | 112.6(3) | O(7)-C(8)-C(7) | 116.0(3) |
| O(1)-Cr-N(1) | 84.0(1) | Cr-O(7)-C(8) | 114.6(2) | O(1)-C(2)-O(2) | 124.5(4) | O(8)-C(8)-C(7) | 119.5(3) |
| O(1)-Cr-N(2) | 96.8(1) | Cr-N(1)-C(1) | 107.4(2) | O(1)-C(2)-C(1) | 115.9(3) | N(1)-C(9)-C(10) | 114.3(3) |
| O(3)-Cr-O(5) | 87.0(1) | Cr-N(1)-C(5) | 104.3(2) | O(2)-C(2)-C(1) | 119.5(3) | N(1)-C(9)-C(14) | 197.3(3) |
| O(3)-Cr-O(7) | 91.9(1) | Cr-N(1)-C(9) | 105.6(2) | N(2)-C(3)-C(4) | 112.5(3) | C(10)-C(9)-C(14) | 112.8(3) |
| O(3)-Cr-N(1) | 94.4(1) | C(1)-N(1)-C(5) | 111.0(3) | O(3)-C(4)-O(4) | 124.4(3) | C(9)-C(10)-C(11) | 109.8(3) |
| O(3)-Cr-N(2) | 84.4(1) | C(1)-N(1)-C(9) | 113.7(3) | O(3)-C(4)-C(3) | 117.4(3) | C(10)-C(11)-C(12) | 110.0(3) |
| O(5)-Cr-O(7) | 112.9(1) | C(5)-N(1)-C(9) | 114.1(3) | O(4)-C(4)-C(3) | 118.3(3) | C(11)-C(12)-C(13) | 110.0(3) |
| O(5)-Cr-N(1) | 80.9(1) | Cr-N(2)-C(3) | 107.5(2) | N(1)-C(5)-C(6) | 108.9(3) | C(12)-C(13)-C(14) | 111.4(3) |
| O(5)-Cr-N(2) | 163.7(1) | Cr-N(2)-C(7) | 104.5(2) | O(5)-C(6)-O(6) | 124.0(4) | N(2)-C(14)-C(9) | 106.4(3) |
| O(7)-Cr-N(1) | 165.2(1) | Cr-N(2)-C(14) | 105.6(2) | O(5)-C(6)-C(5) | 116.2(3) | N(2)-C(14)-C(13) | 114.0(3) |
| O(7)-Cr-N(2) | 81.2(1) | C(3)-N(2)-C(7) | 109.6(3) | O(6)-C(6)-C(5) | 119.7(3) | C(9)-C(14)-C(13) | 113.8(3) |
| N(1)-Cr-N(2) | 86.1(1) | | | | | | |

a) At $1-x$, $y$, $1/2-z$. b) At $x$, $1+y$, $z$. c) At $1-x$, $1+y$, $1/2-z$.

in the G rings are considerably different from those in the R rings(average 38.73° for the G rings and average 4.21° for the R rings, as shown in Table 5). These facts indicate that the G-ring chelates are more strained than the R ones, since the ring strain may be evaluated in terms of the torsion anlges as well as the deviation from the sum of the ideal chelate bond angles for five-membered rings.[20] On the other hand, the quinquedentate edta-type Cr(III) complexes such as [Cr($H_2O$)-(Hedta)] exhibit a sum of the G-ring chelate bond angles similar to that for the cydta complex, but the Cr-O(G) bond (1.935—1.959 Å) is found to be shorter than that (1.99 Å) in the sexadentate edta complex.[21] There seems to be no correspondence between the G-ring strain and the Cr-O(G)-bond lengthening. Hence, it is probable that the cooperation of the chelate-ring strain and the Cr-O(G)-bond lengthening results in the lability to the dissociation of the G-ring chelates in the sexadentate edta and cydta Cr(III) complexes.

In general, the sexadentate edta complexes are less stable than the cydta complexes, forming the quinquedentate edta complexes with an uncoordinated G-ring acetate and one coordinated water molecule more readily than the cydta complexes.[3-5,7-14] This difference in stability of the G-ring chelates between these complexes may be brought about by a small change in the structure of the edta sub-unit around the Cr(III) ions; e.g., the O(G)-Cr-O(G) angles of the cydta Cr(III) complex is smaller by 1.4° than that of the edta complex. Another possible explanation for it is a steric interaction between the R rings and the cyclohexane backbone, a stereochemical requirement or steric compression responsible for the increased ring-closure rates of the cydta complexes over those of the edta ones, as has been discussed in connection with the kinetic differences between the cydta and edta complexes.[4a,5b,22] The present X-ray analaysis substantiates this possibility; short intramolecular nonbonding H-H distances (1.90 Å) are found betweeen the glycinate methylene groups in the R ring and the

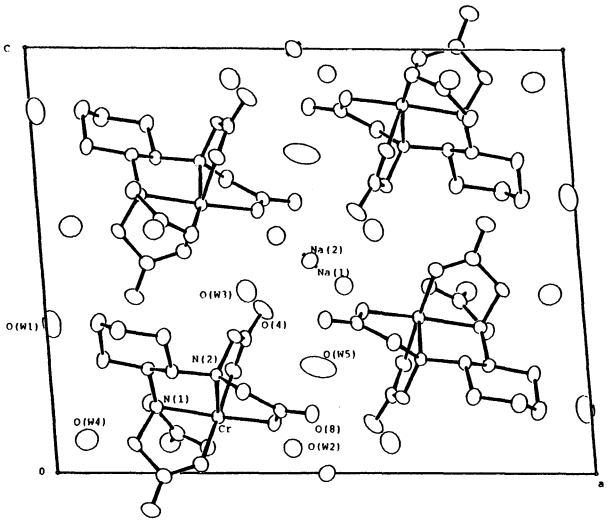


Fig. 2. Crystal structure of Na[Cr(cydta)]·4.5$H_2O$ viewed down the b-axis. All hydrogen atoms are omitted for clarity. Na(2) at (1/2, 1/2, 1/2) overlaps just above Na(1) at (1/2, 0, 1/2) in this plane.

Table 4. Averaged Bond Lengths and Angles within the Complex Anion

| Bond type | No. of bonds | Ring type | Av. length/Å | R.m.s. deviation/Å |
|---|---|---|---|---|
| $C_9$-$C_{14}$ | 1 | E, CH | 1.534 | 0.005 |
| $C_{11}$-$C_{12}$ | 1 | CH | 1.514 | 0.006 |
| C-C | 4 | CH | 1.529 | 0.005 |
| C-C | 4 | G, R | 1.522 | 0.004 |
| C-N | 6 | E,G,R | 1.502 | 0.005 |
| C-$O_c$ | 2 | R | 1.287 | 0.004 |
| C-$O_c$ | 2 | G | 1.295 | 0.004 |
| C-$O_u$ | 2 | R | 1.229 | 0.004 |
| C-$O_u$ | 2 | G | 1.225 | 0.004 |
| Cr-O | 2 | R | 1.951 | 0.003 |
| Cr-O | 2 | G | 1.992 | 0.003 |
| Cr-N | 2 | E | 2.058 | 0.003 |

| Ring type | Bond angle | Mean values (degree) | R.m.s devation (degree) |
|---|---|---|---|
| CH | C-C-C($C_{14}$-$C_9$) | 113.3 | 0.3 |
| | C-C-C($C_{10}$-$C_{13}$) | 110.6 | 0.3 |
| | C-C-C($C_{11}$-$C_{12}$) | 110.0 | 0.3 |
| E | Cr-N-C | 105.6 | 0.2 |
| | N-C-C | 106.9 | 0.3 |
| | N-Cr-N | 86.1 | 0.1 |
| R | Cr-O-C | 115.6 | 0.2 |
| | O-C-C | 116.7 | 0.3 |
| | C-C-N | 112.6 | 0.2 |
| | C-N-Cr | 107.5 | 0.2 |
| | N-Cr-O | 84.2 | 0.1 |
| | C-C-$O_u$ | 118.9 | 0.3 |
| | O-C-$O_u$ | 124.1 | 0.3 |
| G | Cr-O-C | 114.0 | 0.3 |
| | O-C-C | 116.1 | 0.3 |
| | C-C-N | 108.5 | 0.3 |
| | C-N-Cr | 104.4 | 0.3 |
| | N-Cr-O | 81.1 | 0.1 |
| | C-C-$O_u$ | 119.6 | 0.3 |
| | O-C-$O_u$ | 124.3 | 0.4 |
| E-R | C-N-C | 114.5 | 0.3 |
| E-G | C-N-C | 113.8 | 0.3 |
| R-G | C-N-C | 110.3 | 0.3 |

CH, E, R, and G stand for cyclohexane, diamine chelate, and the R and G rings of the acetate chelates, respectively. The subscripts c and u refer to coordinated and uncoordinated oxygen atoms respectively.

methylene groups in the 3 and 6 positions of the cyclohexane ring: C(1)-H(2) and C(10)-H(9) or C(3)-H(4) and C(13)-H(15), as is shown in Fig. 1.

The cyclohexane ring takes the chair conformation, and its bond lengths and angles agree with those found for cydta complexes of six-coordinate Mn(III), Cu(II), and seven-coordinate Fe(III).[1,2,23] The torsion angles for the C-C-C-C chains in the cyclohexane ring range from 47 to 63° in absolute value, with a mean magnitude of 54.28°, approximating those of other cydta complexes.[1,2]

**The Crystal Structure.** A projection of the structure of $Na[Cr(cydta)]\cdot 4.5H_2O$ down the b-axis is shown in Fig. 2. There are two inequivalent sodium ions in the unit cell. Each sodium ion is surrounded by six oxygens in an octahedral configuration; for Na(1) at (1/2, 0, 1/2), four from uncoordinated oxygens of carboxylates in the anions and two from water molecules, and for Na(2) at (1/2, 1/2, 1/2), two from uncoordinated carboxylates and four from water molecules. The octahedral environment around the Na(2) is more deformed than that around the Na(1). The average Na(1)-O and Na(2)-O distances are 2.389 and 2.467 Å respectively. The values of the former bond are shorter than the range observed for the other $Na(O)_6$ polyhedra, but the latter one is within this range. The interbond angles of the $Na(O)_6$ polyhedra have mean deviations from the ideal octahedral values of 0.887° and 9.62° for Na(1) and Na(2) ions respectively. A cationic layer at around 1/2 with the Na(1) and Na(2) polyhedra, linking four and two complex anions respectively, is formed by hydrogen bonds between two crystalline water molecules, O(W5) and O(W2), the oxygen-oxygen distance of which is 2.892 Å. Consequently, this array of sodium ions combines two layers of the complex anions by forcing the hydrophilic moieties of the anions to be directed toward the cations. Hence, it seems to minimize contacts between the hydrophobic cyclohexane rings of the anions in the unit cell. Similar cationic arrangements in the unit cells are observed for $K[Mn(cydta)]\cdot H_2O$[1] and $Ca[Fe(H_2O)(cydta)]_2\cdot 8H_2O$.[23]

Table 5. Selected Torsion Angles (/°)

| | |
|---|---|
| Cr-N(1)-C(1)-C(2) | 1.1(4) |
| Cr-N(2)-C(3)-C(4) | 4.8(3) |
| Cr-N(1)-C(5)-C(6) | 37.8(4) |
| Cr-N(2)-C(7)-C(8) | 39.7(3) |
| C(1)-C(2)-O(1)-Cr | 24.0(4) |
| C(3)-C(4)-O(3)-Cr | 16.7(4) |
| C(5)-C(6)-O(5)-Cr | 12.1(4) |
| C(7)-C(8)-O(7)-Cr | 3.3(4) |
| N(1)-C(1)-C(2)-O(1) | 14.5(5) |
| N(1)-C(5)-C(6)-O(5) | 18.8(4) |
| N(2)-C(3)-C(4)-O(3) | 7.3(4) |
| N(2)-C(7)-C(8)-O(7) | 26.0(4) |
| Cr-N(1)-C(9)-C(14) | 43.1(3) |
| C(9)-C(14)-N(2)-Cr | 44.9(3) |
| N(1)-C(9)-C(14)-N(2) | 59.9(3) |

## References

1) S. J. Rettig and J. Trotter, *Can. J. Chem.*, **51**, 1303 (1972).

2) A. Fuertes, C. Miravitlles, E. Escriva, E. Coronado, and D. Beltran, *J. Chem. Soc., Dalton Trans.*, **1986**, 1795.

3) E. Erickson, D. C. Young, F. F.-L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *Inorg. Chem.*, **10**, 441 (1971).

4) a) D. S. Everhart and R. F. Evilia, *Inorg. Chem.*, **16**, 120 (1977); b) R. F. Evilia, *ibid.*, **24**, 2076 (1985).

5) a) O. W. Howarth, P. Moore, and N. Winterton, *J. Chem. Soc., Dalton Trans.*, **1974**, 2271; b) O. W. Howarth, P. Moore, and N. Winterton, *ibid.*, **1975**, 360.

6) J. Stein, J. P. Fackler, Jr., G. J. McClune, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, **18**, 3511 (1979).

7) W. D. Wheeler and J. I. Legg, *Inorg. Chem.*, **23**, 3798 (1984); W. D. Wheeler and J. I. Legg, *ibid.*, **24**, 1292 (1985).

8) S. Kaizaki and H. Mizu-uchi, *Inorg. Chem.*, **25**, 2732 (1986).

9) N. Miura, M. Shimura, and H. Ogino, *Bull. Chem. Soc., Jpn.*, **60**, 1349 (1987).

10) H. Ogino and M. Shimura, *Adv. Inorg. Bioinorg. Mech.*, **4**, 107 (1986); K. Kanamori and K. Kawai, *Inorg. Chem.*, **25**, 3711 (1986).

11) Y. Kushi, K. Morimasa, and H. Yoneda, Presented at the 49th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1984; Abstract 1N31.

12) R. Herak, G. Srdanov, M. I. Djuran, D. J. Radanović, and M. Bruvo, *Inorg. Chim. Acta*, **83**, 55 (1984).

13) D. Mootz and H. Wunderlich, *Acta Crystallogr., Sect. B*, **36**, 445 (1980).

14) R. T. Helm, W. H. Watson, R. D. Radanović, and B. E. Douglas, *Inorg. Chem.*, **16**, 2351 (1977).

15) S. Kaizaki, M. Byakuno, M. Hayashi, J. I. Legg, K. Umakoshi, and S. Ooi, *Inorg. Chem.* **26**, 2395 (1987).

16) N. Tanaka, K. Kanno, T. Tomita, and A. Yamada, *Inorg. Nucl. Chem. Lett.*, **7**, 953 (1971).

17) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson (1978). MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. University of York, England, and Louvain, Belgium.

18) "International Tables for X-ray Crystallography," Kynoch Press: Birmingham, England, 1974, Vol. IV.

19) "UNICS,", Crystallographic Society of Japan, 1969, C. K. Johnson, "ORTEP II," Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

20) a) H. A, Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959); b) F. Pavelcik, *J. Coord. Chem.*, **13**, 299 (1984).

21) a) G. D. Falton and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, **30**, 1987 (1974); b) L. E. Gerdom, N. A. Baebzinger, and H. M. Goff, *Inorg. Chem.*, **20**, 106 (1980).

22) W. H. Woodruff, B. A. Burke, and D. W. Margerum, *Inorg. Chem.*, **13**, 2573 (1974).

23) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, **88**, 3228 (1966).