

Structure of Disodium *cis*-Bis(iminodiacetato)cobalt(II) Hexahydrate

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Received 4 September 1995

The crystal structure of $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 6\text{H}_2\text{O}$ (Hida = iminodiacetato) contains discrete units $[\text{Co}(\text{Hida})_2]^{2-}$, ions Na^+ , and water molecules. The pseudooctahedral coordination of Co(II) is created by four O atoms (the bond lengths Co—O are 0.202(1), 0.203(1), 0.207(1), and 0.210(1) nm) and two N atoms of two Hida ligands (bond lengths Co—N are 0.211(2) and 0.214(2) nm). The cations Na^+ are pseudooctahedrally surrounded by four water O atoms and two carboxyl O atoms from the different units $[\text{Co}(\text{Hida})_2]^{2-}$.

Complexes of iminodiacetic acid (H_3id a) with the transition metals have been widely investigated both in the solution and solid state. The anion of iminodiacetic acid Hida = $[\text{HN}(\text{CH}_2\text{COO})_2]^{2-}$ belongs among tridentate ligands which can be coordinated to the central atom through two carboxyl groups and one nitrogen atom. The acid-base and complexing properties are involved in the reviews, *e.g.* [1] or are even used as examples for presentation and testing of titration and data treatment procedures [2]. The results of investigations in solution have shown formation of species in the mole ratio metal:ligand = 1:1 and 1:2 [3].

A number of the prepared complexes were studied in solid state and structures of several complexes were determined. The best known 1:1 complex is $\text{Cu}(\text{Hida})_2 \cdot 2\text{H}_2\text{O}$. Its structure showed a polymeric character with the bidentate coordination of the carboxylic groups [4]. Structures of the 1:2 complexes with metals of the first transition row are mostly monomeric, with the monodentate coordination of both the carboxylic groups and nitrogen atom in the *trans*-facial position as was found in $\text{K}_2[\text{Cu}(\text{Hida})_2] \cdot \text{H}_2\text{O}$ [5], $\text{Cs}_2[\text{Ni}(\text{Hida})_2] \cdot 4\text{H}_2\text{O}$ [6], $\text{Li}_2[\text{Ni}(\text{Hida})_2] \cdot 4\text{H}_2\text{O}$ [6], $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 7\text{H}_2\text{O}$ [7] or $\text{Ca}[\text{Co}(\text{Hida})_2]_2 \cdot 6\text{H}_2\text{O}$ [8]. This type of coordination sphere was also observed for $[\text{Ba}_2(\text{H}_2\text{id})_2(\text{H}_2\text{O})_{10}]$ $[\text{Cu}(\text{Hida})_2]$ [9]. Only for $\text{K}_2\text{Zn}(\text{Hida})_2 \cdot 3\text{H}_2\text{O}$ [10] and slow-kinetic $\text{K}[\text{Co}(\text{Hida})_2]$

$\cdot 2.5\text{H}_2\text{O}$ [11] the *cis*-position of the ligands was observed.

For the 1:2 complexes, the influence of the external cation M' on the formation of compounds of the $M'_2[M''(\text{Hida})_2]$ type where M'' is Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and M' is H^+ , Li^+ , Na^+ , K^+ was studied [12]. In systems with Co^{2+} , the external cation influences the oxidizability of $[\text{Co}(\text{Hida})_2]^{2-}$ with oxygen. This effect was observed during the preparation of the Co(II) complexes and it led to the study of $[\text{Co}(\text{Hida})_2]^-/[\text{Co}(\text{Hida})_2]^{2-}$ redox systems and of the stability of aqueous solutions of $M'\text{Co}(\text{Hida})_2$ [13]. The pH dependence of the redox potential values indicates that atmospheric oxygen cannot oxidize the complexes that have already been formed. However, the absorption spectra of aqueous solutions prepared from the initial substances, *i.e.* iminodiacetic acid, alkali carbonate, and cobalt(II) chloride, exhibit the increasing content of $[\text{Co}(\text{Hida})_2]^-$ species (the Co(III) fraction) from 20 % for Li^+ to 75 % for Cs^+ salts. This effect was explained by the same way as with the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ systems, *i.e.* by the assumption of bridge formation between the complex anions through the alkali metal [14].

It is very difficult to confirm this assumption in a solution. On the other hand, in a concentrated solution, we can suppose structures similar to the ones in a solid. Therefore, we decided to solve the struc-

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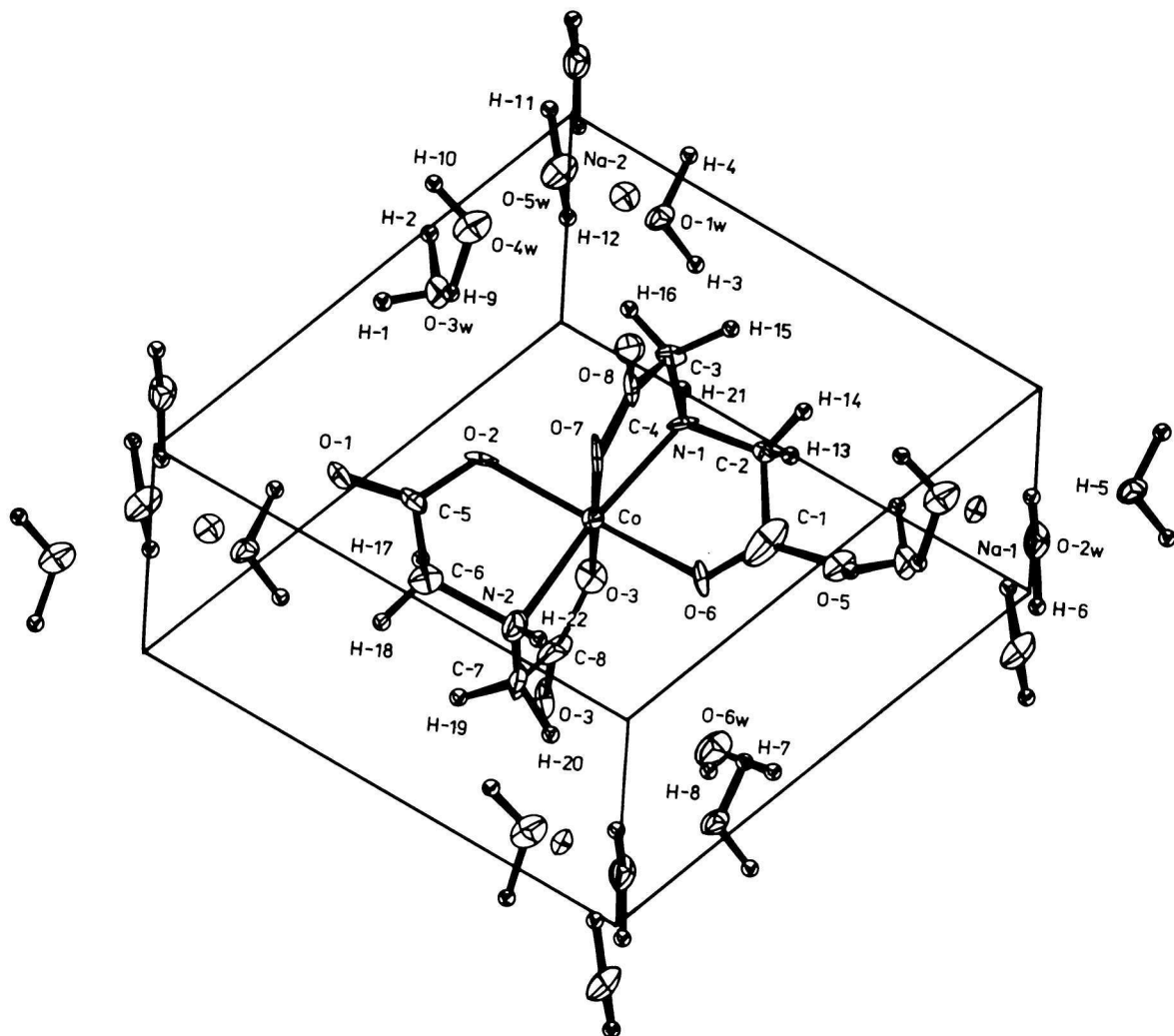


Fig. 1. Unit cell content of the crystal structure of $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 6\text{H}_2\text{O}$.

ture of $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 6\text{H}_2\text{O}$ with the aim to explain possible interactions of the coordination spheres of cobalt atoms. The above-mentioned structure of $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 7\text{H}_2\text{O}$ [7] belonged only to the preliminary results and was not sufficient for detailed considerations.

EXPERIMENTAL

The crystals of $\text{Na}_2[\text{Co}(\text{Hida})_2] \cdot 6\text{H}_2\text{O}$ were prepared according to the previous paper [13]. X-Ray structure analysis:

Crystal data: $\text{C}_8\text{H}_{24}\text{N}_2\text{O}_{14}\text{Na}_2\text{Co}$, $M_r = 477.2$, triclinic, $a = 0.5228(1)$ nm, $b = 0.8908(4)$ nm, $c = 1.0611(1)$ nm, $\alpha = 85.89(6)^\circ$, $\beta = 76.50(7)^\circ$, $\gamma = 83.10(8)^\circ$, $Z = 1$, $D_m = 1.678(7)$ g cm $^{-3}$, $D_x = 1.66$ g cm $^{-3}$, space group P1, $\text{MoK}\alpha$ radiation, $\lambda = 0.07069$ nm, $\mu = 10.1$ cm $^{-1}$, $F(000) = 247.0$.

The yellow coloured crystal with the dimensions

of 0.2 mm \times 0.2 mm \times 0.5 mm was scanned on a SYNTEX P2 $_1$ diffractometer. Intensities were measured with a $\theta/2\theta$ scan technique, $2\theta_{\text{max}} = 55^\circ$. The structure was solved by the deconvolution of the Patterson function using the program XFPS-87 [15]. The E-statistics showed clearly the noncentrosymmetric space group P1. The structure was refined by the least-squares method (241 parameters) based on F -values using the program SHELX76 [16]. The hydrogen atom positions were estimated from the difference Fourier maps, but not refined. Atomic scattering factors (f' and f'') for neutral atoms were obtained from *International Tables for X-Ray Crystallography* [17].

Absorption corrections were applied by the program DIFABS [18]. After the anisotropic refinement final $R = \sum ||\text{Fo}| - |\text{Fc}|| / \sum |\text{Fo}| = 0.053$ and $R_w = [\sum (\text{Fo} - \text{Fc})^2 / \sum w\text{Fo}^2]^{1/2} = 0.053$ for the 1601 observed structure factors; $w = 1.0 / [\sigma^2(\text{Fo}) + (0.001)\text{Fo}]$. The maximal $\Delta\sigma = 0.02$. The maximal and minimal

Table 1. Final Atomic Coordinates with e.s.d.'s in Parentheses and Equivalent Isotropic Thermal Parameters
$$B_{eq} = 4/3 \sum_i \sum_j B_{ij} a_i a_j$$

Atom	$x \cdot 10^3$	$y \cdot 10^3$	$z \cdot 10^3$	$B_{eq}/10^{-2}$ nm
Co	0	500	500	1.65(3)
Na-1	-199(2)	-20(8)	896(6)	2.6(2)
Na-2	205(2)	19(7)	-898(6)	1.9(2)
N-1	207(3)	682(1)	524(1)	2.0(3)
N-2	754(4)	328(2)	489(1)	3.7(5)
O-1	321(3)	201(1)	214(1)	2.9(4)
O-2	273(2)	391(1)	347(1)	2.5(3)
O-3	146(2)	347(1)	628(1)	2.3(3)
O-4	68(3)	115(1)	733(1)	2.2(3)
O-5	665(3)	794(1)	776(1)	2.0(3)
O-6	729(3)	608(1)	642(1)	4.7(5)
O-7	877(3)	656(1)	372(1)	3.7(5)
O-8	941(3)	861(1)	258(1)	3.0(3)
O-1w	-175(3)	161(1)	1064(1)	2.3(3)
O-2w	-587(3)	131(1)	900(1)	2.9(4)
O-3w	509(1)	5545(7)	1077(8)	2.4(2)
O-4w	182(3)	-175(1)	-1046(1)	3.9(4)
O-5w	606(3)	-152(1)	-895(1)	3.0(3)
O-6w	389(2)	450(1)	815(1)	3.8(2)
C-1	-190(5)	707(3)	691(2)	4.9(7)
C-2	868(3)	757(2)	635(1)	1.9(3)
C-3	218(4)	787(2)	407(2)	2.1(5)
C-4	-14(3)	774(2)	341(2)	2.6(5)
C-5	191(4)	-719(2)	-696(2)	2.6(5)
C-6	888(4)	269(2)	348(2)	2.7(4)
C-7	797(4)	217(2)	591(2)	3.1(6)
C-8	14(4)	-770(2)	-346(2)	3.7(6)

difference electron densities are 390 nm^{-3} and -720 nm^{-3} . All the calculations were performed on a PC 386 computer.

RESULTS AND DISCUSSION

The structure of the anionic complex and the arrangement of the units in the unit cell are shown in Fig. 1. The atomic parameters of non-H atoms are given in Table 1. Within the anionic unit, the central atom Co(II) is coordinated by four carboxylic O atoms and two N atoms of two tridentate Hida ligands. The bond lengths and the bond angles are listed in Tables 2 and 3. The donor atoms form a slightly deformed octahedron around Co(II). The chelate rings of both iminodiacetate ligands are essentially nonplanar. The torsion angles of all chelate rings are listed in Table 4. The mean bond lengths Co—N and Co—O (0.213(2) nm and 0.203(1) nm) are very close to the mean values of the same bonds in the heptahydrate form [7] (0.2157(6) nm and 0.208(1) nm), but significantly longer than the mean values in $\text{K}[\text{Co}(\text{Hida})_2] \cdot 2.5\text{H}_2\text{O}$ [11] (0.1942(6) nm and 0.1889(8) nm). Compared with the structure of

Table 2. Bond Distances with e.s.d.'s in Parentheses

Bond	Distance	Bond	Distance
	10^{-1} nm		10^{-1} nm
Co—O-2	2.10(1)	O-1—C-5	1.25(2)
Co—O-3	2.07(1)	O-2—C-5	1.27(2)
Co—O-6	2.02(1)	O-3—C-8	1.29(2)
Co—O-7	1.93(1)	O-4—C-8	1.32(2)
Co—N-1	2.11(1)	O-5—C-1	1.27(2)
Co—N-2	2.14(2)	O-6—C-1	1.22(3)
Na-1—O-4	2.32(1)	O-7—N-1	1.80(2)
Na-1—O-5	2.43(2)	O-7—C-3	1.42(2)
Na-1—O-1w	2.52(1)	O-7—C-4	1.27(2)
Na-1—O-2w	2.29(2)	O-8—C-4	1.17(2)
Na-1—O-4w	2.46(2)	N-1—C-2	1.38(2)
Na-1—O-5w	2.49(1)	N-1—C-3	1.49(2)
Na-2—O-1	2.29(2)	N-2—C-6	1.60(2)
Na-2—O-8	2.38(1)	N-2—C-7	1.45(2)
Na-2—O-1w	2.33(2)	C-1—C-2	1.54(3)
Na-2—O-2w	2.38(1)	C-3—C-4	1.55(3)
Na-2—O-4w	2.45(2)	C-5—C-6	1.55(3)
Na-2—O-5w	2.44(1)	C-7—C-8	1.46(3)

$[\text{Ba}_2(\text{H}_2\text{ida})_2(\text{H}_2\text{O})_{10}][\text{Cu}(\text{Hida})_2]$ [9] (bond lengths Cu—N and Cu—O are 0.2005(5) ($2 \times$) nm and 0.1948(5) ($2 \times$) nm, 0.2548(4) ($2 \times$) nm, respectively) in the present structure the deformation of a coordination polyhedron around Co(II) is more remarkable in bond angles than in distances. Within the sum of ionic radii [19] every cation Na^+ is surrounded by six O atoms of four water molecules and two carboxylic O atoms of different units $[\text{Co}(\text{Hida})_2]^{2-}$ in the vertices of deformed octahedrons (Fig. 2). The mean bond lengths Na-1—Ow, Na-1—O, Na-2—Ow, and Na-2—O (0.244(4) nm, 0.237(2) nm, 0.240(3) nm, and 0.234(2) nm) do not differ significantly from the mean bond length of the same kind in the heptahydrate form. The shortest Na-1...Na-2 separation is 0.344(1) nm. The structural units are mutually linked *via* hydrogen bonds, listed in Table 5. In Fig. 2, the contact of two different octahedra around the ions Na-1 and Na-2 bridged by water molecules is plotted. The bond valence sums around both ions calculated by the formulae for bond valence $s = \exp[-(R - R_0)/B]$ (R is the interatomic distance, R_0 and B are constants) [20] are 1.09 and 1.01. The bond valence sum around the Co atom calculated by the formula $s = a_1/R + a_2/R^2 + a_3/R^3 + a_4/R^4 + a_5/R^5$ for Co—O and Co—N bonds [21] is 2.27. The analogous structural motif was found for $\text{K}[\text{Co}(\text{Hida})_2] \cdot 2.5\text{H}_2\text{O}$ [11] with $\text{K} \cdots \text{K}$ separation 3.86×10^{-1} nm. The bond valence sum around the Co atom of the latter structure is 3.39. In our opinion, the linkage between the cations could be responsible for the transfer of an electron as in case of the mentioned $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ system [14].

Table 3. Bond Angles with e.s.d.'s in Parentheses

Bond angle/°		Bond angle/°	
N-1—Co—N-2	173.8(6)	O-1—Na-2—O-2w	91.5(5)
O-7—Co—N-2	129.1(6)	O-1—Na-2—O-1w	95.2(5)
O-7—Co—N-1	52.7(6)	O-1—Na-2—O-8	107.1(5)
O-6—Co—N-2	93.8(7)	Co—O-2—C-5	115(1)
O-6—Co—N-1	80.0(5)	Co—O-3—C-8	112(1)
O-6—Co—O-7	105.7(5)	Na-1—O-4—C-8	132(1)
O-3—Co—N-2	84.0(5)	Co—O-6—C-1	115(2)
O-3—Co—N-1	97.3(5)	Co—O-7—C-4	126(1)
O-3—Co—O-7	138.9(7)	Co—O-7—C-3	121(1)
O-3—Co—O-6	93.4(5)	Co—O-7—N-1	68.9(6)
O-2—Co—N-2	85.6(5)	C-3—O-7—C-4	70(1)
O-2—Co—N-1	100.5(5)	N-1—O-7—C-4	109(1)
O-2—Co—O-7	73.3(5)	N-1—O-7—C-3	53.3(9)
O-2—Co—O-6	177.9(6)	Co—N-1—O-7	58.5(6)
O-2—Co—O-3	88.6(5)	Co—N-1—C-3	50.0(9)
O-4w—Na-1—O-5w	76.2(5)	O-7—N-1—C-2	136(1)
O-2w—Na-1—O-5w	91.4 (6)	O-7—N-1—C-3	50.0(9)
O-2w—Na-1—O-4w	164.8(6)	O-7—N-1—C-2	136(1)
O-1w—Na-1—O-5w	76.5(4)	Co—N-1—C-3	108(1)
O-1w—Na-1—O-4w	88.0(5)	Co—N-1—C-2	112(1)
O-1w—Na-1—O-2w	80.5(5)	Co—N-1—C-3	110(1)
O-5—Na-1—O-5w	90.6(5)	Co—N-2—C-7	104(1)
O-5—Na-1—O-4w	97.9(6)	Co—N-2—C-6	100(1)
O-5—Na-1—O-2w	90.9(6)	Co—N-2—C-7	112(1)
O-5—Na-1—O-1w	164.3(6)	Na-1—O-1w—Na-2	90.3(5)
O-4—Na-1—O-5w	164.0(6)	Na-1—O-4w—Na-2	88.9(6)
O-4—Na-1—O-4w	92.7(6)	O-5—C-1—O-6	124(2)
O-4—Na-1—O-2w	97.5(5)	O-6—C-1—C-2	121(2)
O-4—Na-1—O-1w	91.9(5)	O-5—C-1—C-2	114(2)
O-4—Na-1—O-5	102.3(5)	N-1—C-2—C-1	110(1)
O-4w—Na-2—O-5w	77.3(5)	O-7—C-3—N-1	77(1)
O-2w—Na-2—O-5w	90.5(5)	O-7—C-3—C-4	50(1)
O-2w—Na-2—O-4w	79.1(5)	O-7—C-4—C-3	122(2)
O-1w—Na-2—O-5w	169.3(5)	O-7—C-4—O-8	147(2)
O-1w—Na-2—O-4w	92.6(6)	O-1—C-5—O-2	125(2)
O-1w—Na-2—O-2w	83.9(5)	O-2—C-5—C-6	116(1)
O-8—Na-2—O-5w	92.0(5)	O-1—C-5—C-6	118(1)
O-8—Na-2—O-4w	83.1(5)	N-2—C-6—C-5	115(1)
O-8—Na-2—O-2w	161.0(6)	N-2—C-7—C-8	119(2)
O-8—Na-2—O-1w	90.4(6)	O-4—C-8—C-7	116(2)
O-1—Na-2—O-5w	94.1(6)	O-3—C-8—C-7	120(2)
O-1—Na-2—O-4w	167.1(7)	O-3—C-8—O-4	124(2)

Table 4. Torsion Angles of Chelate Rings with e.s.d.'s in Parentheses

Torsion angle/°		Torsion angle/°	
Co—O-7—C-4—C-3	115(2)	Co—O-3—C-8—C-7	2(2)
N-1—C-3—C-4—O-7	-48(1)	N-2—C-7—C-8—O-3	7(3)
Co—N-1—C-3—C-4	25(2)	Co—N-2—C-7—C-8	-11(2)
Co—N-1—C-2—C-1	-12(2)	Co—N-2—C-6—C-5	31(2)
O-6—C-1—C-2—N-1	4(3)	O-2—C-5—C-6—N-2	-32(2)
C-2—C-1—O-6—Co	7(3)	Co—O-2—C-5—C-6	14(2)

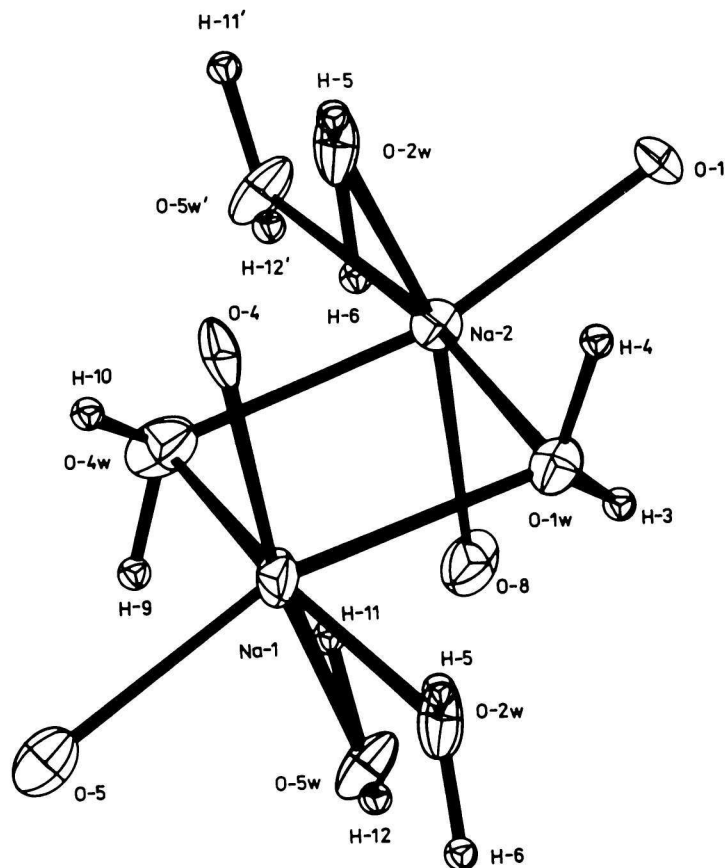
Fig. 2. Na⁺ cations surroundings in the crystal structure of Na₂[Co(Hida)₂] · 6H₂O.

Table 5. Hydrogen Bond Interactions

D—H···A	D···A/10 ⁻¹ nm	H···A/10 ⁻¹ nm	D—H···A/10 ⁻¹ nm
O-4w—H-9···O-5w	3.05(2)	2.35(1)	115.4(9)
O-1w—H-3···O-1 ^a	2.74(2)	2.40(1)	95.8(9)
O-2w—H-5···O-4 ^b	2.83(2)	2.35(1)	104.3(8)
O-2w—H-5···O-6w ^b	2.92(1)	2.128(8)	126.3(7)
O-2w—H-6···O-4 ^b	2.83(2)	2.51(1)	95.2(7)
O-2w—H-6···O-4w ^b	3.08(2)	2.38(2)	120.2(8)
O-5w—H-12···O-8 ^c	2.67(2)	2.24(2)	101.3(8)
O-6w—H-8···O-2w ^d	2.92(1)	2.19(1)	122.3(7)
O-5w—H-12···O-3w ^e	2.72(2)	2.357(8)	97.5(7)

a) $x - 1, y, z + 1$; b) $x - 1, y, z$; c) $x, y - 1, z + 1$; d) $x + 1, y, z$; e) $x - 1, y - 1, z + 1$.

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Translated by F. Valach