mit dort 91,1 (1)°, in der hier vorgestellten Struktur 80,74 (4)°. Dieser durch die Ligandengeometrie bedingte ungünstig kleine Cd—S—P- winkel führt zu einer deutlichen Vergrößerung des Cd—S-Bindungsabstandes auf 2,998 (1) Å. Die Cd—Cl- und Cd—N- Abstände sind demgegenüber in beiden Strukturen von ähnlicher Größe und vergleichbar denen in anderen Cd-Komplexen (Engelhardt & Renz-Kreikebohm, 1989; man vergleiche die dort gegebene Zusammenstellung). Die durch die Koordination des Schwefels am Cadmium-Zentralatom erzwungene Boot-Konformation des sechsgliedrigen P(N—N)₂Cd-Chelatringes führt zu nahezu ekliptischen Anordnungen um die N—N-Bindungen mit sehr kleinen Interplanarwinkeln (Torsionswinkeln) PNNCd und CNNC (Tabelle 2) und zu einem bemerkenswert kurzen Cd—P-Kontaktabstand von nur 3,295 (1) Å. Die Pyrazolidin-Ringe besitzen eine schwach gewellte, klassische Briefumschlag-Konformation. Die ungünstigen ekliptischen Substituentenanordnungen um die N—N-Bindungen dürften mit für die relativ großen N—N-Bindungsabstände von rund 1,47 Å verantwortlich sein. Schwache Kontakte bestehen innerhalb der Ketten über NH···Cl-Wechselwirkungen: N(2)—H(1)···Cl(1^i) mit rCl(1^i)···H(1) 2,89 (3) und rN(2)···Cl(1^i) 3,266 (3) Å sowie zwischen den Ketten über: N(4)—H(7)···Cl(2^{ii}) mit rH(7)···Cl(2^{ii}) 2,62 (4)

und N(4)···Cl(2^{ii}), 3,479 (3) Å [(i) $1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (ii) $1 - x$, $1 - y$, $-z$].

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Structure of the Hydrogen-Bonded Binuclear Complex Trisodium Trihydrogen Bis[tris(glycolato)aluminate(III)]

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Abstract. Na₃H₃[Al(C₂H₂O₃)₃]₂, $M_r = 570 \cdot 2$, cubic, $P4_132$, $a = 12 \cdot 872$ (2) Å, $V = 2133$ (1) Å³, $Z = 4$, $D_x = 1 \cdot 782$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 3 \cdot 0$ cm⁻¹, $F(000) = 1160$, $T = 295$ K. The structure has been refined to $R = 0 \cdot 029$ for 530 unique reflections with $I > 2 \cdot 0\sigma(I)$ and 64 variables. The nearly octahedral 1:3 Al^{III}–glycolate complex has facial geometry. Half of the hydroxy sites are deprotonated, leading to a very short symmetrical hydrogen bond between twofold related hydroxy sites with O···O = 2·425 (4) Å, and the bridging H atom on the twofold axis. Three such hydrogen bonds connect two *fac* Al^{III}–glycolate complexes into a binuclear complex along a common threefold axis. The binuclear complexes are packed into three dimensions by O···Na interactions. The Na atom is coordinated to the O atoms of the carboxylate group to give a highly distorted octahedron.

Introduction. Recently, the coordination of Al^{III} with glycolic acid in aqueous solution was studied with the use of high-field multinuclear NMR (Venema, Peters & van Bekkum, 1990). The results showed that the glycolate ligand coordinates *via* both the carboxylate and the hydroxy groups to the Al^{III} ion. In solution, 1:1, 1:2, 1:3 and polynuclear Al^{III}–glycolate complexes were observed. Moreover, it was found that, in aqueous Al^{III} solutions, deprotonation of the hydroxy moiety of glycolate may occur at pH 4.

^{27}Al MAS and ^{13}C CP/MAS NMR, employed on the powdered single crystals of $Na_3H_3[Al(C_2H_2O_3)_3]_2$, pointed to a highly symmetric 1:3 Al^{III}–glycolate complex. A solid-state structure analysis of this Al^{III}–glycolate complex, obtained from aqueous solution at pH 4, might provide additional information. Therefore, this X-ray structure analysis was started. Preliminary results have been presented elsewhere (Venema, van Koningsveld, Peters & van Bekkum, 1990). Full results are reported in this paper.

Experimental. A solution of $AlCl_3.6H_2O$ (2·5 g, 0·01 mol) and glycolic acid (2·4 g, 0·03 ml) in 25 cm^3 water was adjusted to pH 4 by adding a concentrated solution of NaOH. Samples of this solution were used for a liquid diffusion experiment with ethanol as the precipitating solvent (Orvig, 1985). An excellent, octahedrally shaped, single crystal (approximate dimensions $0·2 \times 0·2 \times 0·4$ mm) of $Na_3H_3[Al(C_2H_2O_3)_3]_2$ was selected. Intensities were measured on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo $K\alpha$ radiation. Cell dimensions were obtained from the setting angles of 25 reflections ($10·8 \leq \theta \leq 13·0°$). Space group $P4_132$ (or $P4_332$) from extinctions ($h \neq 4n$), intensity distribution and second harmonic generation; choice confirmed by successful refinement. Absolute configuration not determined. Intensity data of 686 reflections ($2\theta_{max} = 60·0°$; $0 \leq h \leq k \leq l \leq 18$) with the $\omega/2\theta$ scan mode, $\Delta\omega = (1·0 + 0·35\tan\theta)°$. Three reference reflections measured every two hours showed no significant decay during the 27 h of X-ray exposure time. 530 reflections had $I \geq 2·0\sigma(I)$. No correction was made for absorption effects. The structure was solved by combined Patterson and Fourier techniques. The site symmetries of Al, Na and of one H (participating in hydrogen bonding) are 3(c), 2(d) and 2(d), respectively. Full-matrix least-squares refinement on F of positional and anisotropic thermal parameters of the non-H atoms and isotropic H atoms converged at $R = 0·029$, $wR = 0·028$ ($w = 1$) and $S = 0·6$ for 64 variables and 630 observations [530 with $I > 2·0\sigma(I)$ plus those for which $F_c > F_o$]. The average and maximum shift/ e.s.d. were 0·006 and 0·024, respectively. The final ΔF

synthesis was featureless with $\rho < 0·22$ e Å^{-3}. All calculations were performed on the Delft University Amdahl 470/V7B computer using the programs of $XRAY72$ (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Scattering factors for Al, O, C and Na$^+$ were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. The atomic coordinates with their equivalent isotropic thermal parameters are given in Table 1.* Bond lengths and angles are summarized in Table 2. Fig. 1, drawn with the threefold axis nearly perpendicular to the plane of the paper, shows the molecular conformation and atom labeling in the 1:3 Al^{III}–glycolate complex.

The Al atom occupies a position on the threefold axis and is coordinated to six O atoms from three facial (threefold-related) glycolate ligands, forming a (distorted) octahedron. Half of the hydroxy sites are deprotonated, leading to a very short symmetrical hydrogen bond between twofold-related hydroxy sites with $O\cdots O = 2·425$ (4) Å and the bridging H atom at the 2 axis. Three such hydrogen bonds connect two *fac* Al^{III}–glycolate complexes into a binuclear complex along a common 3 axis. The binuclear complexes are packed into three dimensions by $O\cdots Na$ interactions. The Na coordination is given in Table 2 and shown in Fig. 2. The Na atom is coordinated to the O(1) and O(2) atoms of the carboxylate group to give a highly distorted octahedron. The O(1) atom is coordinated to one Na, while O(2) occupies a bridging position between two Na atoms.

The facial geometry of the glycolate ligands is consistent with the results obtained from solid-state ^{27}Al and ^{13}C NMR experiments. The deprotonation of half of the hydroxy groups is in agreement with the results of the NMR study on the aqueous solution from which the crystal was isolated. The pH (4) of that solution is in the middle of the pH range (3–5) in which ionization of the hydroxy group occurs. The strong hydrogen bond in the present structure represents a rare type of hydrogen bonding in metal–ligand complexes. In the Al^{III}–glycolate complex, the metal is only indirectly involved in the formation of the strong hydrogen bond: the Al^{III} facilitates the ionization of the hydroxy group of glycolate.

Few comparable examples of cooperative hydrogen bonding in metal–ligand complexes are known from the literature. In the bis[tris(1-hydroxybenzene-

Table 1. *Fractional atomic coordinates and (equivalent) isotropic thermal parameters* ($\mathring{A}^2$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}
Al	-0.02284 (8)	-0.02284^*	-0.02284^*	0.0180 (3)
Na	0.2552 (1)	0.1250*	0.0052*	0.0308 (8)
O1	0.1164 (2)	0.0144 (2)	-0.0501 (2)	0.025 (1)
O2	0.2681 (2)	-0.0403 (2)	-0.1076 (2)	0.035 (1)
O3	0.0187 (2)	-0.1513 (2)	-0.0805 (2)	0.023 (1)
C1	0.1749 (3)	-0.0530 (3)	-0.0919 (3)	0.024 (2)
C2	0.1205 (3)	-0.1529 (3)	-0.1212 (4)	0.034 (2)
H21	0.128 (5)	-0.160 (5)	-0.194 (5)	0.08 (2)
H22	0.156 (4)	-0.210 (4)	-0.104 (4)	0.05 (2)
H3	-0.039 (5)	-0.211^*	-0.125^*	0.13 (4)

* Restricted parameter.

Table 2. *Interatomic distances* ($\mathring{A}$) *and bond angles* (°)

Hydrogen-bond values are indicated by an asterisk.

Al coordination		Glycolate ligand	
Al—O(1)	1.888 (3)	C(1)—O(1)	1.269 (5)
Al—O(3)	1.889 (3)	C(1)—O(2)	1.228 (5)
O(1)—Al—O(3)	83.1 (1)	C(1)—C(2)	1.511 (6)
O(1)—Al—O(1)^i	89.0 (1)	C(2)—O(3)	1.411 (5)
O(1)—Al—O(3)^i	169.4 (1)	C(2)—H(21)	0.95 (6)
O(1)—Al—O(3)^{ii}	98.0 (1)	C(2)—H(22)	0.89 (5)
O(3)—Al—O(3)^i	90.9 (1)	O(3)—H(3)	1.21 (4)*
		O(3)···O(3)^{iii}	2.425 (4)*

Na coordination			
Na—O(1)	2.392 (3)	Al—O(1)—C(1)	117.9 (2)
Na—O(2)	2.581 (3)	O(1)—C(1)—O(2)	123.9 (4)
Na—O(2)^{iv}	2.284 (3)	O(1)—C(1)—C(2)	114.4 (3)
O(1)—Na—O(2)	52.4 (1)	O(2)—C(1)—C(2)	121.6 (4)
O(1)—Na—O(2)^{iv}	174.1 (1)	C(1)—C(2)—O(3)	108.9 (3)
O(1)—Na—O(1)^v	84.8 (1)	C(1)—C(2)—H(21)	106 (4)
O(1)—Na—O(2)^v	95.1 (1)	C(1)—C(2)—H(22)	113 (3)
O(1)—Na—O(2)^{vi}	91.1 (1)	H(21)—C(2)—H(22)	97 (5)
O(2)—Na—O(2)^{iv}	123.9 (1)	C(2)—O(3)—H(3)	113 (2)
O(2)—Na—O(2)^v	138.8 (1)	C(2)—O(3)—Al	114.9 (2)
O(2)—Na—O(2)^{vi}	85.7 (1)	H(3)—O(3)—Al	124 (3)
O(2)^{iv}—Na—O(2)^{vi}	93.3 (1)	O(3)—H(3)—O(3)^{iii}	179 (5)*

Symmetry code: (i) z, x, y; (ii) y, z, x; (iii) $\frac{3}{4} - y, \frac{3}{4} - x, \frac{3}{4} - z$; (iv) $z + \frac{1}{2}, -x + \frac{1}{2}, -y$; (v) $z + \frac{1}{4}, -y + \frac{1}{4}, x - \frac{1}{4}$; (vi) $-y + \frac{1}{4}, x - \frac{1}{4}, z + \frac{1}{4}$.

2-thiolato)stannate] complex, three cooperative hydrogen bonds are observed with O···O distances of 2.465 (9), 2.440 (9) and 2.486 (8) $\mathring{A}$, respectively (Holmes, Shafieezad, Chandrasekhar, Holmes & Day, 1988). No crystallographic symmetry is present within this binuclear complex. The positions of the H atoms in the hydrogen bonds were not determined. In the bis(trisaminoethanolatecobalt) complex (Jones, Rozière & Lehmann 1986), two of the three hydrogen bonds are crystallographically independent [O···O = 2.390 (7) and O—H = 1.195 (4) $\mathring{A}$; O···O = 2.429 (6) and O—H = 1.204 (7) and 1.228 (7) $\mathring{A}$]. The position of the H atom in the shortest (symmetrical) hydrogen bond is constrained by space-group symmetry. These observations, together with the presently reported structure, confirm that a shortening of the O···O distance is accompanied by an increase in O—H bond length, resulting in a symmet-

rical hydrogen bond. This is in excellent agreement with the findings of Misaki, Kashino & Haisa (1989, and references cited therein).
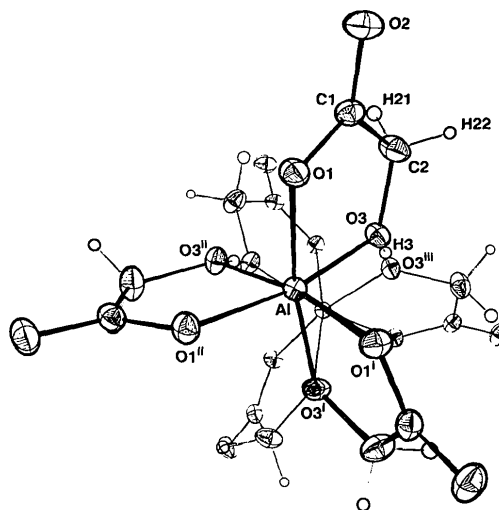
Fig. 1. *ORTEP* drawing of the binuclear Al^{III}-glycolate complex (Johnson, 1965), showing molecular conformation and atom numbering. Symmetry code: see Table 2.
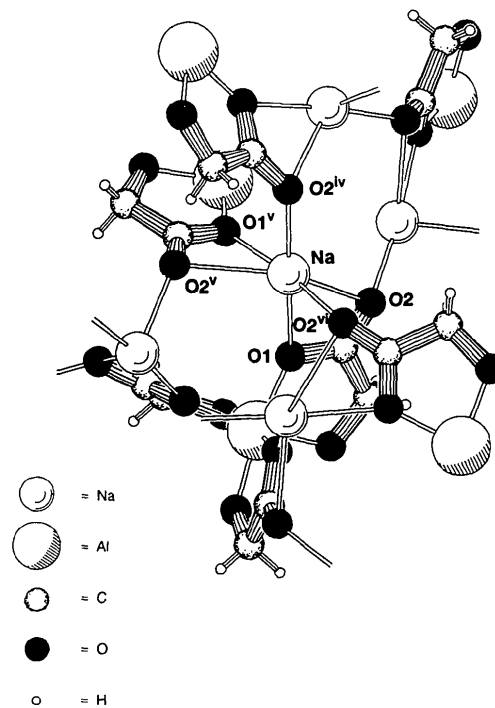

Fig. 2. *PLUTON* drawing (Spek, 1982) of the packing. The Na coordination sphere is highlighted. Symmetry code: see Table 2.

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Structure of cis-Dichloro(dimethyl sulfoxide)(pyridine)platinum(II)

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Abstract. $[PtCl_2(C_2H_6OS)(C_5H_5N)]$, $M_r = 423 \cdot 22$, monoclinic, $P2_1/b$, $a = 8 \cdot 884$ (1), $b = 8 \cdot 784$ (1), $c = 16 \cdot 355$ (3) Å, $\gamma = 113 \cdot 96$ (2)°, $V = 1166 \cdot 3$ (7) Å^3, $Z = 4$, $D_x = 2 \cdot 41$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 127 \cdot 56$ cm^{-1}, $F(000) = 784$, $T = 298$ K, $R = 0 \cdot 050$ for 1500 unique observed reflections. Pt^{II} exhibits a slightly distorted cis square-planar coordination to two Cl and one N atom of the pyridine (py) moiety and to one S atom of the dimethyl sulfoxide (dmso) moiety. The Pt—S distance is 2·209 (4) Å. The observed variations in the Pt—S bond lengths in cis-[Pt(dmso)LCl$_2$] (L = dmso, MeCN, PhCH$_2$CN, py, 2Me-C$_5$H$_4$N, NH$_3$) complexes provide a rare example of the cis influence of the ligands.

Introduction. The pyridine cis effect in Pt^{II} complexes has been widely discussed in the literature (Kukushkin, 1985). But py's position in the sequence of the cis influence of the ligands is unknown. Earlier we found (Moiseev, Kukushkin, Simanova, Belsky & Konovalov, 1989) that the value of the Pt—S bond length in cis-[Pt(dmso)LCl$_2$] (L = dmso, MeCN, 2Me-C$_5$H$_4$N, NH$_3$) complexes is affected mainly by the L cis influence. In this work we have prepared single crystals of the cis-[Pt(dmso)pyCl$_2$] complex

suitable for X-ray analysis and determined the py cis influence.

Experimental. The title compound was prepared by solid-state thermal isomerization of trans-[Pt(dmso)pyCl$_2$] at 420 K (Kukushkin, Moiseev & Sidorov, 1989). Anal. Calc.: Cl, 16·75; Pt, 46·10. Found: Cl, 16·6; Pt, 46·1. IR (KBr pellet, Perkin–Elmer model 983G spectrometer), cm^{-1}: 1608 s ($\nu_{C=C,C=N}$), 1150 and 1141 s (ν_{SO}), 443 m (ν_{PtS}), 376 m (γ_{CSO}), 345 and 318 m (ν_{PtCl}). The colourless rod-like crystals were obtained by recrystallization from boiling acetonitrile by slow cooling of the saturated solution.

Diffraction data collected on a Nicolet P3 diffractometer, using Mo $K\alpha$ radiation, β-filter; cell parameters from refined angles of 12 centered reflections with 2θ between 20 and 24°. 1599 independent reflections of which 1500 with $I \geq 3\sigma(I)$ measured up to $2\theta \leq 50°$ by the $\theta/2\theta$ scan technique. Scan speed 3·4–12° min^{-1}, range of hkl: $h = 0$ to 12, k = −12 to 12, $l = 0$ to 20. Standard reflections 300, 040, 006 measured every 100 reflections showed no change with time. Structure solved by means of Fourier synthesis based on the Pt-atom coordinates obtained from Patterson synthesis and refined by full-matrix