1), the water molecules apparently coming from the crown ether which was not completely dry. There is a strong hydrogen bond, O···O = 2·566 (9) Å, between the water of crystallization, H2O(3), and one of the waters, H2O(2), coordinated to the Zn atom. There are weak hydrogen bonds between the waters and the O atoms of the crowns linking the crowns together in the stacks. The O···O distances range from 2·79 (1) to 2·86 (1) Å which is rather longer than the 2·69 (5) Å found in triaquatetranitrothorium(IV)–18-crown-6 (Rogers, Kurihara & Benning, 1987). The angles at the O atoms involved range from 93 to 132°. This would appear to be the first $ZnI_2(H_2O)_2$ tetrahedron reported in the literature. The mean Zn—I distance, 2·543 (1) Å, is similar to that in other ZnI_2L_2 molecules, *e.g.* 2·552 (1) Å in diiodobis(pyridine)zinc (Le Querler, Borel & LeClaire, 1977), as is the large, 122·2 (5)°, I—Zn—I angle. The mean Zn—O distance is 2·004 (5) Å, which is in the range expected for tetrahedral zinc complexes (Brown & Lewis, 1984, and references therein).

I am indebted to the Danish Science Research Council and to the Carlsberg Foundation for the diffractometer.

References

Brown, C. J. & Lewis, J. F. P. (1984). *Acta Cryst.* C**40**, 368–370.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Hazell, A. C. (1988). *Acta Cryst.* C**44**, 88–92.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Le Querler, J. F., Borel, M. M. & LeClaire, A. (1977). *Acta Cryst.* B**33**, 2299–2300.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Nelmes, R. J. (1975). *Acta Cryst.* A**31**, 273–279.
Paige, C. R. & Richardson, M. F. (1984). *Can. J. Chem.* **62**, 332–335.
Pears, D. A., Stoddart, J. F., Crosby, J., Allwood, B. L. & Williams, D. J. (1986). *Acta Cryst.* C**42**, 51–53.
Rogers, R. D., Kurihara, L. K. & Benning, M. M. (1987). *Acta Cryst.* C**43**, 1056–1058.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1988). C**44**, 447–449

Structure of (2,2′-Bipyridyl)(*N,N*-carboxylatomethylanthranilato)chromium(III) Trihydrate

By K. Swaminathan, U. C. Sinha and C. Chatterjee

Physics Department, Indian Institute of Technology, Bombay 400 076, *India*

R. P. Patel

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, *India*

and V. M. Padmanabhan*

Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, *India*

(*Received* 1 *July* 1987; *accepted* 14 *October* 1987)

Abstract. $[Cr(C_{11}H_8NO_6)(C_{10}H_8N_2)].3H_2O$, M_r = 512·4, monoclinic, $P2_1/n$, a = 9·679 (2), b = 12·831 (1), c = 17·770 (2) Å, β = 98·52 (1)°, V = 2182·60 Å^3, Z = 4, D_x = 1·556, D_m(by flotation) = 1·562 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, graphite monochromator, μ = 6·12 cm^{-1}, $F(000)$ = 1048, room temperature, R = 0·028 with unit weights for 2053 unique reflections. The two N atoms of bipyridyl and the N atom and the three carboxyl O atoms of the quadridentate anthranilic diacetate (atda) moiety give distorted octahedral coordination around Cr. The Cr—N(1) bond distance of the bipyridyl is shorter [2·037 (3) Å] than the other two Cr—N bond distances whereas the Cr—O distances are nearly equal [average 1·933 (3) Å]. The phenyl ring is effectively planar and the *o*-carboxyl group is rotated by 29·6 (2)°. The bipyridyl ring is twisted.

* To whom correspondence should be addressed.

0108-2701/88/030447-03$03.00

Introduction. Aminopolycarboxylate ligands can wrap around the metal ion in different ways. The metal complexes are used for oxidation of small molecules and also as probes in biological systems. The structure determination of the title compound was undertaken to establish the details of the coordination.

Experimental. The complex was synthesized by the literature method (Tomita, Kyuno & Tsuchia, 1969):

$$CrCl_3.6H_2O + \text{atda (aq.)} \rightarrow [Cr(\text{atda})(H_2O)_2] + 3HCl$$

$$[Cr(\text{atda})(H_2O)_2] + \text{bpy (aq.)} \rightarrow [Cr(\text{atda})(\text{bpy})].$$

Recrystallization of the compound from water gave red crystals. Intensity data for 3536 reflections (crystal size $0{\cdot}1 \times 0{\cdot}28 \times 0{\cdot}35$ mm) were collected on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), ω–2θ scan, lattice parameters refined from 25 reflections $5 \leq \theta \leq 12°$, 3 standard reflections recorded every 60 min showed only random deviations: $1 \leq \theta \leq 23{\cdot}5°$, $-10 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 19$. Symmetry-equivalent reflections were averaged. $R_{\text{int}} = 0{\cdot}028$, 2053 unique reflections with $F_o > 3\sigma(F_o)$, Lp correction, no absorption correction. Structure solution by Patterson and Fourier methods. All the H atoms were located from difference maps. Structure refinement by least squares based on F values using anisotropic thermal parameters for non-hydrogen atoms. Number of parameters refined: 395, including H atoms. $R = 0{\cdot}028$, $wR = 0{\cdot}034$, unit weights; $\Delta/\sigma(\text{max.}) = 0{\cdot}78$, $\Delta\rho$ in final difference map $-0{\cdot}2$ to $0{\cdot}3$ e Å^{-3}, C—H distances in the range 0·91 (3)–1·03 (4) Å and O—H distances 0·79 (3)–0·90 (4) Å. Programs *SHELX*76 (Sheldrick, 1976), *PLUTO* (Motherwell & Clegg, 1978), computer NORSK DATA. Atomic scattering factors those of *SHELX*76, for Cr atom from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional parameters are given in Table 1.* Bond distances and angles are listed in Table 2. A *PLUTO* view of the molecule is shown in Fig. 1 and the packing of the molecules in the unit cell in Fig. 3. The chromium atom is six coordinated with a distorted octahedral geometry. The equatorial plane consists of two N atoms of the bipyridyl ligand, the N atom and O atom from one of the acetato groups of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44458 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* Cr $\times 10^5$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Cr	41464 (6)	28153 (4)	32496 (3)	24 (1)
N(1)	5320 (3)	4019 (2)	2945 (2)	29 (3)
N(2)	3577 (3)	4008 (2)	3944 (2)	27 (3)
N(3)	3069 (3)	1460 (2)	3479 (2)	25 (3)
O(1)	2604 (2)	3144 (2)	2458 (1)	32 (2)
O(2)	5545 (2)	2382 (2)	4075 (1)	34 (2)
O(3)	4930 (2)	1874 (2)	2574 (1)	34 (3)
O(4)	399 (3)	3271 (2)	1954 (2)	56 (3)
O(5)	6290 (3)	1001 (2)	4775 (2)	59 (3)
O(6)	5447 (3)	427 (2)	1874 (2)	47 (3)
C(1)	6173 (4)	3955 (3)	2413 (2)	40 (4)
C(2)	7015 (4)	4767 (3)	2262 (2)	47 (5)
C(3)	6999 (4)	5662 (3)	2679 (3)	47 (5)
C(4)	6111 (4)	4251 (3)	3211 (2)	43 (4)
C(5)	5267 (3)	4913 (3)	3333 (2)	30 (3)
C(6)	4246 (4)	4932 (3)	3874 (2)	30 (3)
C(7)	3949 (4)	5799 (3)	4276 (2)	42 (4)
C(8)	2971 (4)	5750 (3)	4762 (2)	46 (5)
C(9)	2316 (4)	4815 (3)	4851 (2)	40 (4)
C(10)	2652 (4)	3963 (3)	4433 (2)	35 (4)
C(11)	1632 (3)	1693 (3)	3602 (2)	29 (4)
C(12)	1041 (4)	1157 (3)	4153 (2)	39 (4)
C(13)	−286 (4)	1407 (4)	4292 (2)	52 (5)
C(14)	−1031 (4)	2193 (4)	3893 (3)	53 (5)
C(15)	−484 (4)	2680 (3)	3318 (2)	44 (3)
C(16)	849 (3)	2446 (3)	3149 (2)	29 (3)
C(17)	1291 (4)	2988 (3)	2478 (2)	35 (4)
C(18)	3970 (4)	962 (3)	4147 (2)	38 (4)
C(19)	5390 (4)	1463 (3)	4343 (2)	35 (4)
C(20)	3036 (4)	804 (3)	2781 (2)	33 (4)
C(21)	4273 (4)	1016 (3)	2373 (2)	32 (4)
O(*W*1)	5693 (3)	1968 (3)	870 (2)	69 (4)
O(*W*2)	3343 (3)	3268 (3)	927 (2)	72 (4)
O(*W*3)	6791 (4)	8010 (3)	4300 (2)	91 (5)

* $U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3(1-\cos^2\beta)$.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cr—N(1)	2·037 (3)	C(11)—C(12)	1·386 (5)
Cr—N(2)	2·091 (3)	C(12)—C(13)	1·381 (6)
Cr—N(3)	2·100 (3)	C(13)—C(14)	1·374 (6)
Cr—O(1)	1·939 (2)	C(14)—C(15)	1·370 (6)
Cr—O(2)	1·927 (2)	C(15)—C(16)	1·400 (5)
Cr—O(3)	1·934 (3)	C(16)—C(11)	1·406 (5)
N(1)—C(5)	1·342 (4)	C(16)—C(17)	1·497 (5)
N(1)—C(1)	1·346 (5)	C(17)—O(1)	1·292 (4)
C(1)—C(2)	1·374 (6)	C(17)—O(4)	1·227 (4)
C(2)—C(3)	1·368 (6)	C(11)—N(3)	1·470 (4)
C(3)—C(4)	1·373 (6)	N(3)—C(18)	1·507 (4)
C(4)—C(5)	1·386 (5)	C(18)—C(19)	1·511 (5)
C(5)—C(6)	1·477 (5)	C(19)—O(2)	1·288 (4)
C(6)—C(7)	1·375 (5)	C(19)—O(5)	1·225 (4)
C(7)—C(8)	1·376 (6)	N(3)—C(20)	1·495 (5)
C(8)—C(9)	1·377 (6)	C(20)—C(21)	1·514 (5)
C(9)—C(10)	1·386 (6)	C(21)—O(3)	1·295 (4)
C(10)—N(2)	1·339 (5)	C(21)—O(6)	1·226 (5)
N(2)—C(6)	1·366 (4)		
N(1)—Cr—N(2)	78·9 (1)	C(9)—C(10)—N(2)	123·2 (3)
N(3)—Cr—O(1)	88·3 (1)	C(10)—N(2)—C(6)	117·9 (3)
N(3)—Cr—O(2)	85·7 (1)	N(2)—C(6)—C(7)	121·1 (3)
N(3)—Cr—O(3)	81·7 (1)	N(2)—C(6)—C(5)	114·6 (3)
N(1)—Cr—O(1)	92·5 (1)	C(11)—C(12)—C(13)	120·3 (4)
N(1)—Cr—O(2)	93·7 (1)	C(12)—C(13)—C(14)	120·6 (4)
N(1)—Cr—O(3)	91·4 (1)	C(13)—C(14)—C(15)	119·3 (4)
N(2)—Cr—N(3)	108·0 (1)	C(14)—C(15)—C(16)	122·2 (4)
N(2)—Cr—O(1)	91·5 (1)	C(15)—C(16)—C(11)	117·5 (3)
N(2)—Cr—O(2)	88·7 (1)	C(16)—C(11)—C(12)	120·0 (3)
O(1)—Cr—O(3)	91·0 (1)	C(11)—C(16)—C(17)	125·6 (3)
O(1)—Cr—O(2)	173·8 (1)	C(16)—C(17)—O(1)	119·5 (3)
N(1)—Cr—N(3)	173·0 (1)	C(16)—C(17)—O(4)	119·4 (3)
N(2)—Cr—O(3)	170·1 (1)	O(1)—C(17)—O(4)	121·1 (3)
N(1)—C(1)—C(2)	122·3 (4)	C(11)—N(3)—C(18)	114·7 (3)
C(1)—C(2)—C(3)	118·4 (4)	N(3)—C(18)—C(19)	113·7 (3)
C(2)—C(3)—C(4)	120·0 (4)	C(18)—C(19)—O(2)	117·1 (3)
C(3)—C(4)—C(5)	119·3 (4)	C(18)—C(19)—O(5)	118·4 (3)
C(4)—C(5)—N(1)	120·8 (3)	O(2)—C(19)—O(5)	124·3 (3)
C(5)—N(1)—C(1)	119·1 (3)	C(11)—N(3)—C(20)	109·4 (2)
C(4)—C(5)—C(6)	123·8 (3)	C(20)—N(3)—C(18)	110·7 (3)
N(1)—C(5)—C(6)	115·4 (3)	N(3)—C(20)—C(21)	112·0 (3)
C(6)—C(7)—C(8)	120·4 (3)	C(20)—C(21)—O(3)	114·3 (3)
C(7)—C(8)—C(9)	118·9 (4)	C(20)—C(21)—O(6)	120·7 (3)
C(8)—C(9)—C(10)	118·5 (4)	O(3)—C(21)—O(6)	124·9 (3)

atda, while the axial positions are occupied by the carboxylic O atom and the O atom of the other acetato group of atda (Fig. 2). The Cr—O bond distances are normal [average 1·933 (2) Å]. The Cr—N distances vary between 2·037 (3)–2·100 (3) Å with Cr—N(1) being the shortest [2·037 (3) Å]. The deviations from the octahedral angles at the Cr atom caused by the bite of the chelate rings [N(1),C(5),C(6),N(2); N(3),-C(20),C(21),O(3); N(3),C(18),C(19)O(2); and N(3),-C(11),C(16),C(17),O(1)] are within 12°. As is to be expected, the angle subtended by these chelate rings at the Cr atom increases with increasing ring size [78·9 (1), 81·7 (1), 85·7 (1), 88·3 (1)° respectively]. The Cr—O(1) bond is tilted by 11·6 (2)° with respect to the best plane with the four in-plane atoms and Cr while the Cr—O(2) bond is tilted by only 4·9 (2)°. The five atoms defining the coordination plane [Cr,N(1),N(2),-N(3), and O(3)] are coplanar within 0·020 (1) Å. The bipyridyl chelate ring atoms are coplanar within 0·033 (2) Å, with the mean plane of the ring being tilted with respect to the metal coordination plane by 2·2°. The pyridine rings are twisted by 6·2 (2)° due to chelation strain as is also indicated by the N(2)—C(6)—C(5)—N(1) torsion angle of 4·8 (1)°. The bond distances and bond angles in the bipyridyl ligand are normal. In general, bond distances and bond angles of the anthranilic ring of atda are nearer the zwitterion values reported in the neutron diffraction study of free anthranilic acid (Brown & Ehrenberg, 1985), in which the neutral molecules and zwitterions have an unusual coexistence. However, the C—O(1) and C—O(4) distances are nearer the values for the neutral species. The phenyl ring is effectively planar with σ(plane), defined as $[\sum_i d_i^2/N-3]^{1/2}$, being 0·030 (3) Å. The immediate substitutions show more deviations from the least-squares plane [N(3): 0·101 (2) and C(17): −0·145 (2) Å]. The mean plane of the carboxyl group [C(17), O(1) and O(4)] is rotated by 29·6 (2)° from the plane of the phenyl ring whereas in the free anthranilic acid it is rotated by 5·38 (4)°. Although Tomita, Kyuno & Tsuchia (1969) isolated the complex as the dihydrate, our density determination indicated the presence of three water molecules which was subsequently confirmed by detailed structure analysis.

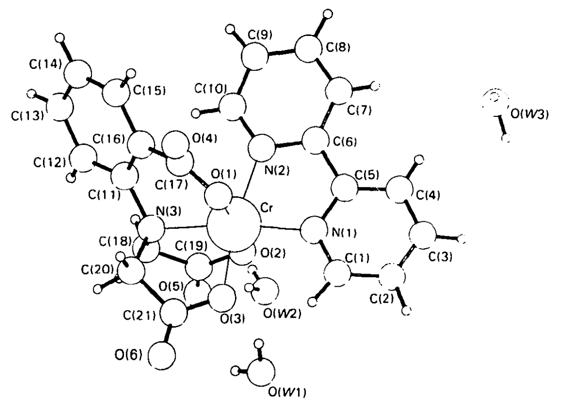

Fig. 1. General view of the molecule.

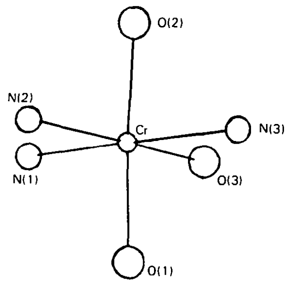

Fig. 2. Cr coordination.

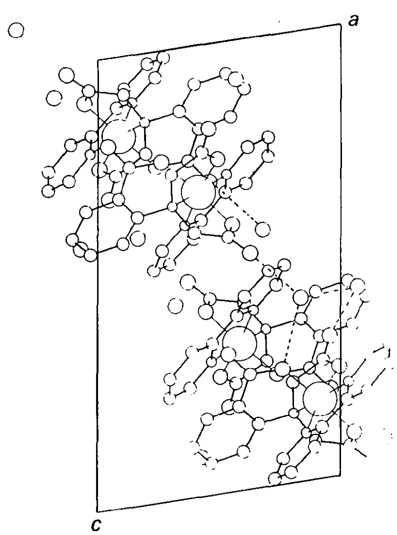

Fig. 3. Packing of the molecules: dashed lines indicate hydrogen bonds.

The possible hydrogen bonds are: O(W1) to atom O(6) and water molecule O(W2) with distances 2·983 (6) and 2·834 (6) Å; O(W2) to atoms O(1) and O(5) with distances 2·918 (6) and 2·795 (6) Å; O(W3) to atom O(4) with a bond distance of 2·859 (4) Å.

We thank Dr T. N. Guru Rao, National Chemical Laboratory, Poona, for sparing the CAD-4 to collect data.

References

BROWN, C. J. & EHRENBERG, M. (1985). *Acta Cryst.* C**41**, 441–443.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TOMITA, T., KYUNO, E. & TSUCHIA, R. (1969). *Bull. Chem. Soc. Jpn*, **42**, 947–951.