Discussion. Fig. 1 shows the geometry of the $[Cu_2F_2\text{-}(dmpz)_6]^{2+}$ cation.

The cations are dimeric, consisting of two $[CuF\text{-}(dmpz)_3]^+$ units related by an inversion centre, and are joined into neutral globular clusters with two BF_4^- anions. The units are connected by two asymmetric fluoro bridges with Cu—F bond lengths 2·166 (6) and 1·876 (6) Å in the ordered molecule. The coordination of the Cu atom may be viewed as square-based pyramidal with an F atom in apical position and a second F atom and three coordinating N atoms at the corners of the square base. The aromatic rings of the ligands are planar. Pyrazole ring [N(11)–C(15)] is almost coplanar with the Cu_2F_2 plane [dihedral angle 2·0 (6)°]. The molecular geometry of the cation closely corresponds to the geometry of the fluoro-bridged copper(II) compounds described by Rietmeyer *et al.* (1984) and Ten Hoedt *et al.* (1981). Relevant data on these compounds are presented in Table 2.

Each N—H atom of the ligands is involved in an asymmetric bifurcated hydrogen bond to the bridging F and one of the F atoms of the BF_4^- anion respectively (Table 2) (see Scheme in *Introduction*). The sums of the angles round the N—H atoms [360 (10)° for H(11), 354 (10)° for H(21) and 355 (10)° for H(31)] illustrate the planar geometry of the bifurcated hydrogen bonds. The boron atoms and the two bridging fluorine ions of a dimer lie on a straight line parallel to the c axis.

The crystal structure (Fig. 2) consists of an R-centred unit cell containing 12 dimeric cations and 24 BF_4^- anions. Nine ordered cations are on $\bar{1}$ sites, three disordered cations on $\bar{3}$ sites, 18 BF_4^- anions on general positions and six BF_4^- anions on threefold axes. The relation between the ordered and disordered molecules explains the pseudosymmetry: except for a small rotation angle, 4·0 (6)°, they are translated by $\frac{1}{2}a$. The external pseudo-cube faces (021, $\bar{2}$01, $2\bar{2}$1, angle 91°) correspond to close-packed planes of the globular molecules which form an approximate cubic close packing.

Part of this work (ALS) was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization
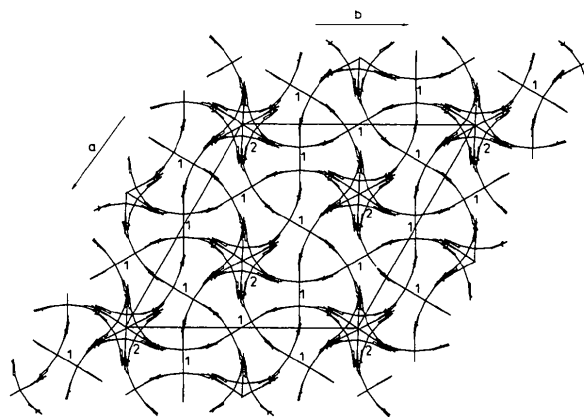

Fig. 2. A view of the unit-cell contents down the c axis showing all possible orientations of the disordered molecules superimposed. The ordered cations are marked with 1 and the disordered cations are marked with 2. From this illustration it is clear that the disordered molecules can occupy all three orientations without disrupting the packing of the molecules in the crystal. The BF_4^- anions that project to positions coinciding with the centre of the molecule have been omitted for clarity.

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The Na⁺ Complex of the Ionophore A204A

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Abstract. $Na[C_{49}H_{83}O_{17}].C_3H_6O$, $M_r = 1025$, monoclinic, $C2$, $a = 27\cdot223$ (7), $b = 14\cdot529$ (3), $c = 14\cdot369$ (3) Å, $\beta = 91\cdot18$ (2)°, $V = 5682$ Å^3, $Z = 4$, $D_x = 1\cdot19$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot848$ cm^{-1}, $F(000) = 2220$, $T = 295$ K, $R = 0\cdot066$ for 5340 observed data. A previously reported deter-

mination of the structure of the Na–A204A complex [Jones, Chaney, Chamberlin, Hamill & Chen (1973). *J. Am. Chem. Soc.* **95**, 3399–3400] indicated anomalously long Na$^+$···O coordination distances. This structure is essentially isomorphous to that previously reported, but the Na$^+$···ligand distances are normal.

Introduction. Ionophores are compounds that induce or facilitate ion transport across membranes. The resultant changes in ion gradients and trans-membrane potentials influence a wide spectrum of biological activities. Their usefulness depends upon their ion selectivity and efficiency of transport. The ion selectivity must be largely influenced by the relative binding energies of the different cations. Among the factors influencing this are cation size and charge, number, type and distribution of ligands, and the flexibility of the ionophore. However, the relative importance of these parameters is disputed.

The antibiotic A204A (Fig. 1) is a biologically active compound produced by a strain of *Streptomyces albus*. It induces monovalent cation permeability and exhibits selectivity for K$^+$ over Na$^+$. A204A is a member of the family of monocarboxylic acid polycyclic polyether antibiotics. Crystal structures of the free acid (Smith, Strong & Duax, 1978) and of the Na$^+$ and Ag$^+$ complexes (Jones, Chaney, Chamberlin, Hamill & Chen, 1973) of A204A have been reported. However, the anomalously long metal–ligand distances reported in the Na$^+$ complex, 0·3 Å longer than reported for other Na···O coordination distances, has called into question the identity of the cation in this complex (Dobler, 1981). Since an accurate knowledge of the coordination distances is necessary for an evaluation of the binding of the various cations to a particular ionophore, a redetermination of the structure of the Na–A204A complex was undertaken.

Experimental. Recrystallized from acetone/water, crystal 0·48 × 0·98 × 0·02 mm; Nicolet *P*3 diffractometer, Nb-filtered Mo *K*α radiation; θ–2θ scans; lattice parameters from 25 reflections with 24 ≤ 2θ ≤ 28°, Lp corrections, no absorption correction; [(sinθ)/λ]$_{max}$ = 0·65 Å^{-1}; 0 ≤ *h* ≤ 35, −1 ≤ *k* ≤ 18, −18 ≤ *l* ≤ 18; 4 standard reflections after every 96 data, ±3%; intensity data measured and saved as profiles of 96 intervals for each scan; profile intensity data converted into integrated net intensities (Blessing, 1986) and structure-factor amplitudes. 7868 data, 6790 unique, 5340 observed with *I* > 2σ(*I*); the coordinates of the previously reported structure were used as a starting set; origin fixed with the Na atom; $\sum w(|F_o| - |F_c|)^2$ minimized; H atoms of the ionophore skeleton at calculated positons, H atoms of −OH and −CH$_3$ not included; 619 parameters consisting of a scale factor, 212 positional, 402 anisotropic thermal factors, 4 isotropic thermal factors for solvent atoms; *R* = 0·066

and 0·079, *wR* = 0·090 and 0·093 for observed and all data respectively; *S* = 2·4; *w* = (1/σ$_F^2$), σ$_F$ as defined by Stout & Jensen (1968) with an instability correction of 0·05; (Δ/σ)$_{max}$ = 0·5; max. and min. heights in final difference Fourier synthesis ±0·4 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs used included the Enraf–Nonius (1979) *Structure Determination Package* and *ORTEP* (Johnson, 1965).*

Discussion. Refinement was limited by the large number of weak reflections [48·5% with *I* < 3σ(*I*)]. Final positional parameters are found in Table 1, the atom-numbering scheme is shown in Fig. 1 and the coordination of the Na–A204A complex is illustrated in Fig. 2. Bond lengths and angles are unexceptional.

Two intramolecular hydrogen bonds are observed, both of which involve the O(2) atom of the carboxylic acid. One of these to the hydroxyl O(3) (2·57 Å) orients the carboxyl group so that O(1) is in position to coordinate to the cation. The other hydrogen bond from O(2) to hydroxyl O(15) of ring *A* (2·66 Å) is the usual head-to-tail connection observed in antibiotics of this nature which serves to form the cavity in which the cation is coordinated.

As noted above, the anomalously long metal–ligand distances reported by Jones *et al.* (1973) in their determination of the Na–A204A complex led to the questioning of their identification of the cation. A comparison of the metal–ligand distances found in this study and those previously reported is found in Table 2. While the average distance (2·57 Å) found in the Na–A204A complex is longer than that found in the Na$^+$ complexes of monensin (2·43 Å) (Duax, Smith & Strong, 1980), nigericin (2·24 Å) (Barrans, Alléaume & David, 1980) or X206 (2·54 Å) (Van Roey, Duax, Strong & Smith, 1984), it is 0·2 Å less than that reported by Jones *et al.* (2·79 Å) for Na–A204A. Similarly, there is a correspondence of the shortest Na–ligand distance found here (2·34 Å) to those found in monensin (2·35 Å), nigericin (2·24 Å), and X206 (2·38 Å) as opposed to that reported by Jones *et al.* in Na–A204A (2·71 Å). The cation was misidentified in the report of Jones *et al.* Preliminary results indicate that the complex reported by Jones *et al.* corresponds to the K$^+$ complex (Pangborn, Duax & Langs, in preparation).

A comparison of the torsion angles of this structure with those of the free acid and the metal complex reported by Jones *et al.* (1973) reveals that the conformation of the antibiotic is maintained in all these

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* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43661 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structures with only subtle changes. If the torsion angles of ring G, which is not involved in the cation coordination, are excluded, the average difference between corresponding torsion angles in the Na+ complex and the metal complex of Jones et al. is 2°, and the maximum difference is 7°.

Table 1. Atomic coordinates of Na—A204A.acetone

	x	y	z
Na	0·69853 (7)	0·0000	0·2615 (1)
C(1)	0·6655 (3)	0·1513 (4)	0·1392 (4)
C(2)	0·6533 (2)	0·2525 (4)	0·1145 (3)
C(2A)	0·6958 (2)	0·3163 (5)	0·1337 (4)
C(3)	0·6062 (2)	0·2805 (3)	0·1663 (3)
C(4)	0·5900 (2)	0·3801 (4)	0·1515 (3)
C(4A)	0·5736 (2)	0·4008 (5)	0·0509 (3)
C(5)	0·5490 (1)	0·4055 (3)	0·2188 (3)
C(6)	0·5641 (1)	0·3831 (3)	0·3211 (3)
C(6A)	0·6033 (2)	0·4486 (4)	0·3555 (3)
C(6B)	0·4816 (2)	0·3435 (5)	0·3730 (5)
C(7)	0·5807 (2)	0·2811 (3)	0·3251 (3)
C(8)	0·6006 (2)	0·2505 (4)	0·4193 (3)
C(9)	0·6169 (2)	0·1505 (3)	0·4177 (3)
C(10)	0·5753 (2)	0·0803 (4)	0·4156 (4)
C(11)	0·5957 (2)	−0·0164 (4)	0·4183 (4)
C(11A)	0·5853 (3)	−0·0781 (8)	0·2674 (6)
C(12)	0·6327 (2)	−0·0282 (3)	0·4988 (3)
C(12A)	0·6551 (2)	−0·1235 (4)	0·5013 (4)
C(13)	0·6703 (2)	0·0507 (3)	0·5033 (3)
C(14)	0·7042 (2)	0·0502 (4)	0·5886 (3)
C(14A)	0·6812 (3)	0·0809 (5)	0·6804 (4)
C(15)	0·7459 (2)	0·1110 (3)	0·5560 (3)
C(15A)	0·8244 (2)	0·1622 (5)	0·6101 (4)
C(16)	0·7484 (2)	0·0931 (3)	0·4507 (3)
C(16A)	0·7490 (2)	0·1835 (3)	0·3949 (3)
C(17)	0·7903 (1)	0·0311 (3)	0·4232 (3)
C(18)	0·7924 (2)	−0·0670 (3)	0·4611 (3)
C(19)	0·8230 (2)	−0·1171 (4)	0·3897 (3)
C(20)	0·8185 (2)	−0·0582 (3)	0·3018 (3)
C(21)	0·7966 (2)	−0·1036 (3)	0·2160 (3)
C(22)	0·8272 (2)	−0·1821 (4)	0·1779 (3)
C(23)	0·7893 (2)	−0·2400 (4)	0·1259 (3)
C(24)	0·7414 (2)	−0·2234 (4)	0·1793 (3)
C(25)	0·6976 (2)	−0·2056 (4)	0·1175 (3)
C(26)	0·6823 (2)	−0·2881 (4)	0·0555 (4)
C(26A)	0·6665 (3)	−0·3716 (5)	0·1151 (7)
C(27)	0·6426 (2)	−0·2580 (5)	−0·0106 (5)
C(27A)	0·6598 (3)	−0·3696 (8)	−0·1303 (8)
C(28)	0·6582 (2)	−0·1731 (5)	−0·0675 (4)
C(28A)	0·6176 (3)	−0·1446 (8)	−0·1385 (6)
C(29)	0·6722 (2)	−0·0950 (4)	−0·0012 (3)
C(29A)	0·6960 (2)	−0·0137 (5)	−0·0488 (4)
C(30)	0·4917 (2)	0·5291 (4)	0·1833 (3)
C(31)	0·4958 (2)	0·6225 (5)	0·1371 (4)
C(32)	0·5109 (2)	0·6970 (5)	0·2084 (4)
C(33)	0·4764 (2)	0·6939 (4)	0·2881 (4)
C(33A)	0·4649 (3)	0·8356 (8)	0·3702 (9)
C(34)	0·4752 (2)	0·5989 (4)	0·3309 (3)
C(34A)	0·4395 (3)	0·5902 (6)	0·4098 (5)
O(1)	0·7075 (2)	0·1306 (4)	0·1681 (3)
O(2)	0·6316 (2)	0·0944 (4)	0·1289 (5)
O(3)	0·5669 (1)	0·2227 (3)	0·1407 (2)
O(4)	0·6196 (1)	0·2678 (2)	0·2615 (2)
O(5)	0·5396 (1)	0·5015 (3)	0·2101 (2)
O(6)	0·5241 (1)	0·3980 (3)	0·3839 (2)
O(7)	0·6190 (1)	−0·0400 (3)	0·3334 (3)
O(8)	0·6463 (1)	0·1366 (2)	0·5011 (2)
O(9)	0·7893 (1)	0·0895 (3)	0·6083 (2)
O(10)	0·7034 (1)	0·0434 (2)	0·4276 (2)
O(11)	0·7867 (1)	0·0171 (2)	0·3242 (2)
O(12)	0·7503 (1)	−0·1444 (3)	0·2378 (2)
O(13)	0·6251 (2)	−0·3315 (4)	−0·0693 (4)
O(14)	0·7094 (1)	−0·1274 (3)	0·0624 (2)
O(15)	0·6298 (1)	−0·0695 (3)	0·0465 (3)
O(16)	0·4604 (1)	0·5334 (3)	0·2603 (3)
O(17)	0·4937 (2)	0·7576 (4)	0·3578 (3)
C(S1)	0·4614 (7)	0·085 (2)	0·183 (2)
C(S2)	0·4390 (8)	0·173 (2)	0·141 (1)
C(S3)	0·4831 (9)	0·025 (2)	0·115 (2)
O(S1)	0·4585 (6)	0·073 (1)	0·257 (2)

Since there is no significant conformational change between these structures, the relative conformational energies of these should be approximately equal and therefore should not make a major contribution to the ion selectivity. Because ion binding should be the major factor in selectivity the empirical bond-length:bond-strength equation of Brown & Shannon (1973) would be expected to be most valid in this case. This equation is of the form $s = (R/R_0)^{-N}$ and relates the bond strengths with the cation ligand distance R. The values R_0 and N have been determined from the coordination geometries of various cations with oxygen ligands available in the literature such that the average value of the total bond strength, $S = \Sigma s$, for the reference complexes equals one. Thus, for a given complex of a univalent ion a value $S < 1$ indicates weaker than average binding while $S > 1$ indicates stronger than average binding. The literature values of R_0 and N for Na+ are 1·622 and 4·3 (Brown & Wu, 1976). When applied to the A204A complex, one obtains relative bond strengths of 0·96 for the Na+ complex. This indicates a below-average binding affinity of A204A Na+, an ion for which this ionophore is not selective.
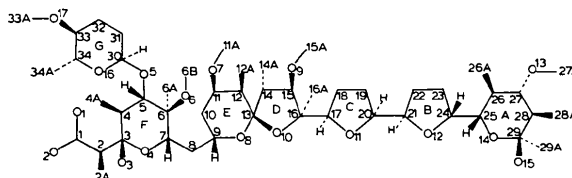

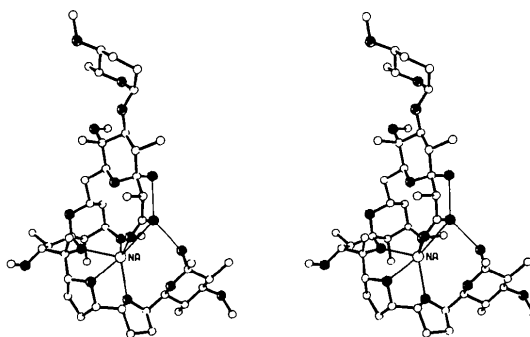Fig. 1. Chemical structure of A204A and the numbering scheme.

Fig. 2. Observed conformation of Na—A204A illustrating the coordination of the cation and the intramolecular H bonds.

Table 2. Na+–ligand distances (Å)

This study		Jones et al.
2·339	Na⋯O(1)	2·713
2·949	O(2)	2·970
2·487	O(7)	2·721
2·469	O(10)	2·737
2·558	O(11)	2·853
2·555	O(12)	2·790
3·425	O(14)	3·122
3·718	O(15)	3·167

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Structure of Bis(cyclopentadienyl)bis(pyridine)cadmium(II)

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Abstract. $[Cd(C_5H_5)_2(C_5H_5N)_2]$, $M_r = 400.80$, monoclinic, $P2_1/n$, $a = 12.79$ (1), $b = 10.093$ (4), $c = 14.38$ (1) Å, $\beta = 107.20$ (8)°, $V = 1773$ (2) Å^3, $Z = 4$, $D_x = 1.501$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 12.3$ cm^{-1}, $F(000) = 808$, $T = 294$ K, $R = 0.0326$ for 2407 observed reflections with $I > 2\sigma(I)$. The Cd atom is pseudo-tetrahedrally coordinated by the two N atoms of the pyridine molecules and by two C atoms of the η^1-bonded Cp moieties.

Introduction. Bis(cyclopentadienyl)cadmium [Cd(Cp)$_2$] was prepared to compare its reactivity with the related [Zn(Cp)$_2$] as part of an investigation on the reactions of (cyclopentadienyl)zinc compounds with Ni^0 complexes (Budzelaar, Boersma, van der Kerk, Spek & Duisenberg, 1985a,b; Fischer, Boersma, Kojić-Prodić & Spek, 1985). Single crystals of the present pyridine complex were obtained by slow crystallization from pyridine. An X-ray study of this complex was undertaken in order to establish the molecular geometry of the first known example of a cyclopentadienyl–Cd

compound. A preliminary report of this study was given previously (Fischer, van Mier, Boersma, Smeets & Spek, 1987).

Experimental. Yellowish crystal 0.58 × 0.25 × 0.20 mm suitable for X-ray diffraction was sealed under nitrogen in a Lindemann-glass capillary. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation, cell constants from the angular settings of 25 reflections with $16.3 < \theta < 20.4°$. Intensity data of 4074 unique reflections were collected within a quarter of the reflection sphere: $0 \le h \le 16$; $0 \le k \le 13$; $-18 \le l \le 17$; $(\sin\theta)/\lambda < 0.65$ Å^{-1}; $\omega/2\theta$ scan mode with $\Delta\omega = (0.70 + 0.35\tan\theta)°$. Three reference reflections [200 (e.s.d. $= 0.64\%$); 020 (e.s.d. $= 0.51\%$); 002 (e.s.d. $= 0.68\%$)], measured every hour showed a linear decay of 0.2% during the 77 hours of X-ray exposure time. The intensity data were corrected for this decay and for Lorentz–polarization effects. No correction for absorption was applied in view of the small intensity variation of 6% about the mean of the 360° ψ scan of the 404 reflection. Standard deviations in the intensities were increased according to an analysis of the variance

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