

- RYAN, R. R. & SWANSON, B. I. (1974). *Inorg. Chem.* **13**, 1681–1684.
 SLATER, J. C. (1964). *J. Chem. Phys.* **41**, 3199–3204.
 SWANSON, B. I. & RYAN, R. R. (1973). *Inorg. Chem.* **12**, 283–286.
 VON DREELE, R. B. & CHEETHAM, A. K. (1974). *Proc. Roy. Soc. A* **338**, 311–326.
 VON DREELE, R. B., EYRING, L., BOWMAN, A. L. & YARNELL, J. L. (1975). *Acta Cryst.* **B31**, 971–974.
 WOLBERG, A. (1969). *Acta Cryst.* **B25**, 161–162.

Acta Cryst. (1977). **B33**, 52–59

The Crystal and Molecular Structures of Cs^+ Complexes of Tetranactin and Nonactin

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The structure of the Cs^+ -tetranactin complex [space group $P2_1/n$, $Z = 4$, $a = 16.022$ (6), $b = 20.418$ (10), $c = 15.671$ (8) Å, $\beta = 89.46^\circ$ (4)] was deduced from the structure of the isomorphous Rb^+ complex and refined to an R index of 5.8% including H atoms. That of the Cs^+ -nonactin complex [space group $P2/n$, $Z = 2$, $a = 16.073$ (2), $b = 10.126$ (1), $c = 14.417$ (2) Å, $\beta = 96.09^\circ$ (1)] was solved by the Patterson method. The R index was 4.6% including H atoms. In these complexes, the average distances $\text{Cs}^+ \cdots \text{O}(\text{carbonyl})$ are longer than $\text{Cs}^+ \cdots \text{O}(\text{ether})$. Comparison of the structures with the other alkali-metal complexes shows that the nonactin molecule is more deformable than that of tetranactin, and the cavity in the tetranactin molecule seems to reach its maximum size in the Cs^+ complex. The crystal structure of the Cs^+ -nonactin complex is a new type which has never before been found in the alkali-metal complexes of nactins.

Introduction

Macrotetrolide nactins (nonactin and its homologues including tetranactin) are ionophorous antibiotics which exhibit high cation selectivity in complex formation with alkali-metal ions (Pioda, Wachter, Dohner & Simon, 1967). In an aqueous acetone solution, the formation constant of the K^+ complex of the nactins is larger by as much as 100 times than that of the Na^+ complex. The difference was interpreted by the smaller hydration energy of K^+ ($\Delta G_H^\circ = -76.5$ kcal mol $^{-1}$) compared with that of Na^+ (-96.5 kcal mol $^{-1}$) (Prestegard & Chan, 1970). However, in spite of the larger difference in ΔG_H° between Cs^+ (-62 kcal mol $^{-1}$) and Na^+ , the formation constants of the two nactin complexes in an aqueous solution are comparable (Eisenman, Krasne & Ciani, 1975), which may indicate the presence of a conformational strain in the Cs^+ complexes. Furthermore, the order of selectivity against Na^+ and Cs^+ in tetranactin is the reverse of that in nonactin (Eisenman *et al.*, 1975). In proton NMR spectra, the chemical shift of the methine proton H1(C7) in the Cs^+ -nonactin com-

plex (Cs^+ -NNC)* was apparently different from those of K^+ -NNC and Na^+ -NNC (Prestegard & Chan, 1970), and in far-IR spectra, a characteristic stretching vibration band of the $\text{Cs}^+ \cdots \text{O}$ bond was observed at a lower frequency region than that of the $\text{K}^+ \cdots \text{O}$ bond (Ivanov *et al.*, 1973).

In the present paper, the crystal and molecular structures of Cs^+ -NNC and Cs^+ -TNC are compared with those of K^+ -NNC, Na^+ -NNC, K^+ -TNC and Na^+ -TNC, which were previously reported (Dobler, Dunitz & Kilbourn, 1969; Dobler & Phizackerley, 1974; Sakamaki, Iitaka & Nawata, 1976).

Experimental

Cs^+ -NNC and Cs^+ -TNC were prepared in a methanol solution containing approximately equal molar amounts of the nactins and CsSCN . The com-

* Hereafter the alkali-metal complexes of nonactin and tetranactin are abbreviated as M^+ -NNC and M^+ -TNC respectively.

plexes, crystallized from ethyl acetate-acetone (1:1, v/v), were not so brittle as the K^+ and Na^+ complexes. Diffraction intensities were measured on a Philips PW 1100 diffractometer with $Cu K\alpha$ radiation (graphite-monochromated) by the $\theta-2\theta$ scanning method. No absorption correction was applied. Lattice parameters were determined by least-squares calculation of the angular settings for 18 reflexions automatically centred on the diffractometer (Table 1).

Crystal structure analyses

(a) The crystal structure of Cs^+ -TNC was derived from that of the isomorphous complex Rb^+ -TNC (Sakamaki, Iitaka & Nawata, 1976). Refinement of the structure was carried out by the least-squares method (block-diagonal-matrix approximations) with unit weight. H atoms were found on the difference electron density map, and their parameters were refined assuming isotropic temperature factors. The atomic scattering factors for non-hydrogen atoms were those given in *International Tables for X-ray Crystallography* (1962), and for H those given by Stewart, Davidson & Simpson (1965). The final R index was 5.8%. Estimated standard deviations (e.s.d.'s) for $Cs^+ \cdots O$, C-C bonds and C-C-C angles were 0.008, 0.017 Å and 1.0° respectively.

(b) The heavy-atom method was applied to the crystal structure analysis of Cs^+ -NNC. Although systematic absences indicated the possible space group to be $P2_1/n$ or Pn , the positional parameters of Cs^+ (0.25, 0.1, 0.25) derived from the Patterson function suggested $P2_1/n$. Non-hydrogen atoms were recognized on the electron density map, and no sign of disorder was observed for SCN^- (0.75, y , 0.25). Atomic parameters of the H atoms, recognized on the difference electron density map, were refined with isotropic temperature factors. The final R value was 4.6%. The e.s.d.'s for $Cs^+ \cdots O$, C-C bonds and C-C-C angles were 0.006, 0.012 Å and 0.7° respectively.

Table 1. *Crystal and intensity-measurement data*

	Cs^+ -TNC	Cs^+ -NNC
Formula	$C_{44}H_{72}O_{12}CsSCN$	$C_{40}H_{64}O_{12}CsSCN$
F.W.	984.0	927.4
Crystal system	Monoclinic	Monoclinic
a (Å)	16.022 (6)	16.073 (2)
b (Å)	20.418 (10)	10.126 (1)
c (Å)	15.671 (8)	14.417 (2)
β ($^\circ$)	89.46 (4)	96.09 (1)
U (Å ³)	5126.5	2333.2
Space group	$P2_1/n$	$P2_1/n$
Z	4	2
D_x (g cm ⁻³)	1.274	1.320
μ (Cu $K\alpha$) (cm ⁻¹)	64.5	70.5
Crystal size (mm)	0.23 × 0.23 × 0.30	0.13 × 0.15 × 0.15
2θ max ($^\circ$)	120	120
Number of observed reflexions	3534	2112

Results and discussions

(a) Molecular structure

The atomic numbering is shown in Fig. 1. The final atomic parameters are listed in Table 2.* The interatomic distances and angles, and the internal rotation angles are given in Table 3. The molecular structures of both Cs^+ complexes were essentially identical with those of the other corresponding alkali-ion complexes, in which O atoms of carbonyl and ether groups were arranged tetrahedrally around the central ion and completed the distorted cubic coordination. The geometry of the coordination of the O atoms around Cs^+ is illustrated in Table 4.

In Fig. 2 the distances between ligand O atoms and the central cations found in various alkali-ion complexes of nactins are plotted against the ionic radii of the cations. It is seen that in the Cs^+ complexes, the distances between the central M^+ ions and O atoms are all roughly equal to the sum of the ionic radius of M^+ and the van der Waals radius of O (Pauling, 1960). As shown in Fig. 2, the $M^+ \cdots O$ (carbonyl) distances in all these complexes are close to the sum of ionic radius of M^+ and van der Waals radius of O. Although the $M^+ \cdots O$ (ether) distances are comparable with the $M^+ \cdots O$ (carbonyl) distances in the Cs^+ and Rb^+ complexes, they are, on the other hand, appreciably longer than the latter in the K^+ and Na^+ complexes, which shows that close approach of the O(ether) atoms to M^+ by the intramolecular steric hindrance. Incorporation of a larger ion into the nactin molecule causes an increase in the distances between the O atoms of carbonyl and ether groups, which results in expansion of the molecular cavity. Remarkable conformational differences between the complexes are observed in the in-

* A list of structure factors and the final atomic parameters of the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32017 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

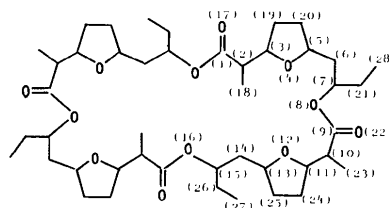


Fig. 1. Structures of tetranactin and nonactin. Atomic numbering is shown for one half of the tetranactin molecule and the asymmetric unit of the nonactin molecule; in the latter C(27) and C(28) are absent. The rest of the tetranactin molecule is expressed by adding 50 to the numbers of the chemically equivalent atoms.

Table 2. Final atomic parameters with estimated standard deviations in parentheses

The positional and thermal parameters for non-hydrogen atoms are multiplied by 10⁴, and those for hydrogen atoms are multiplied by 10³ and 10 respectively. The temperature factors for non-hydrogen atoms are of the form:

$$T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Isotropic temperature factors were given to hydrogen atoms:
 $T = \exp[-B(\sin \theta/\lambda)^2].$



(a) Cs⁺-tetranactin complex

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C 1	5928(6)	3658(5)	2725(7)	57(6)	27(3)	70(7)	-1(3)	0(5)	-2(4)
C 2	5450(8)	3998(6)	3240(8)	81(6)	24(3)	86(9)	1(4)	13(6)	-7(4)
C 3	4520(7)	3998(6)	3240(8)	68(7)	33(4)	102(9)	2(4)	6(6)	6(5)
O 4	4243(4)	3313(3)	3199(5)	65(4)	30(2)	96(5)	2(2)	17(4)	-3(3)
C 5	3393(7)	3268(6)	3513(9)	60(6)	34(4)	118(10)	6(4)	11(6)	-4(5)
C 6	3343(7)	2833(5)	4290(8)	71(7)	40(4)	91(8)	2(4)	27(6)	-6(5)
C 7	3671(7)	2142(5)	4124(7)	76(6)	36(4)	67(7)	-5(4)	8(5)	-4(4)
O 8	3106(4)	1826(3)	3511(5)	60(4)	36(2)	76(5)	3(2)	19(3)	-4(3)
C 9	3431(7)	1525(5)	2825(7)	66(6)	33(4)	56(6)	12(4)	23(5)	11(4)
C10	2781(7)	1184(5)	2320(7)	59(6)	32(4)	71(7)	0(4)	6(5)	-5(4)
C11	2996(7)	1220(5)	1377(7)	73(7)	22(3)	77(7)	2(4)	12(6)	-3(4)
O12	2960(4)	1902(3)	1136(4)	72(4)	28(2)	65(4)	-1(2)	-2(3)	0(2)
C13	2676(7)	1947(5)	248(7)	81(7)	30(3)	56(6)	-7(4)	4(5)	-5(4)
C14	1884(6)	2361(5)	221(6)	64(6)	32(3)	59(6)	-6(4)	-3(5)	15(4)
C15	1991(7)	3067(5)	481(7)	66(6)	38(4)	63(7)	-9(4)	1(5)	2(4)
O16	2564(5)	3357(3)	-146(5)	74(4)	32(2)	65(4)	-7(2)	2(3)	-1(3)
O17	5790(5)	3734(4)	1973(5)	70(4)	45(3)	74(5)	5(3)	-1(4)	7(3)
C18	5785(8)	4676(6)	3531(9)	95(9)	32(4)	124(10)	-1(5)	0(8)	-10(5)
C19	3967(8)	4311(6)	3891(10)	89(8)	38(5)	141(11)	21(5)	29(8)	-12(6)
C20	3124(8)	3979(6)	3694(10)	82(8)	40(5)	158(13)	16(5)	32(8)	1(6)
C21	3656(9)	1732(6)	4947(8)	102(9)	48(5)	74(8)	-5(5)	7(7)	1(5)
O22	4170(4)	1528(4)	2682(4)	57(4)	55(3)	69(5)	9(3)	12(3)	-5(3)
C23	2732(9)	471(6)	2613(8)	113(9)	28(4)	93(9)	-4(5)	13(7)	12(5)
C24	2408(8)	882(5)	783(8)	86(8)	30(4)	77(8)	-3(4)	5(6)	-8(4)
C25	2546(8)	1242(5)	-63(7)	102(8)	32(4)	67(7)	3(4)	-3(6)	-2(4)
C26	1185(7)	3440(6)	480(8)	66(6)	51(5)	85(8)	9(4)	7(6)	-2(5)
C27	1272(9)	4148(7)	727(10)	101(9)	49(5)	121(11)	19(6)	-3(8)	-12(6)
C28	3941(10)	1032(8)	4825(9)	133(12)	64(6)	94(10)	1(7)	-11(9)	17(6)
C31	3216(7)	3699(5)	109(7)	65(6)	24(3)	82(8)	6(4)	-1(5)	-7(4)
C32	3732(8)	3970(5)	-625(8)	84(7)	34(4)	77(7)	-13(4)	3(6)	-2(5)
C53	4642(8)	3940(5)	-417(8)	80(7)	31(4)	100(9)	-8(4)	15(6)	-12(5)
O54	4875(5)	3255(4)	-358(5)	72(4)	39(3)	91(5)	-1(3)	28(4)	2(3)
C55	5746(7)	3168(6)	-611(9)	60(6)	40(4)	103(10)	-6(4)	18(6)	-4(5)
C56	5796(7)	2715(6)	-1381(8)	77(7)	44(4)	88(8)	1(5)	24(6)	-1(5)
C57	5437(8)	2028(6)	-1236(7)	72(7)	48(4)	61(7)	-4(5)	9(6)	0(4)
O58	5967(4)	1714(3)	-584(5)	59(4)	37(3)	73(5)	1(2)	12(3)	0(3)
C59	5604(6)	1435(5)	92(7)	61(6)	36(4)	66(7)	-7(4)	23(5)	-11(4)
C60	6235(7)	1085(5)	635(8)	59(6)	32(4)	83(7)	6(4)	9(5)	-2(4)
C61	5989(7)	1136(5)	1560(7)	79(7)	29(3)	67(7)	6(4)	0(6)	-1(4)
O62	6050(5)	1816(3)	1806(5)	74(4)	30(2)	71(5)	8(3)	-8(3)	-3(3)
C63	6331(7)	1860(5)	2685(7)	67(6)	34(4)	69(7)	6(4)	-1(5)	-6(4)
C64	7115(6)	2219(6)	2712(7)	55(6)	43(4)	66(6)	7(4)	-4(5)	1(4)
C65	7083(6)	2939(5)	2411(7)	58(6)	38(4)	62(6)	4(4)	2(5)	-8(4)
O66	6535(4)	3280(3)	3019(4)	67(4)	32(2)	63(4)	10(2)	-1(3)	-7(3)
O67	3386(5)	3784(4)	851(5)	71(4)	49(3)	70(5)	2(3)	-7(4)	-13(3)
C68	3432(9)	4668(6)	-783(11)	115(10)	32(4)	148(13)	-2(5)	6(9)	18(6)
C69	5243(10)	4224(6)	-1065(10)	130(11)	34(5)	132(11)	-21(6)	44(9)	-3(6)
C70	6050(9)	3847(7)	-856(11)	81(9)	50(5)	150(13)	-11(5)	38(8)	-16(7)
C71	5478(9)	1597(7)	-2046(8)	112(10)	54(5)	65(8)	-3(6)	7(7)	-7(5)
O72	4867(4)	1464(4)	216(5)	59(4)	53(3)	68(5)	-2(3)	16(3)	-2(3)
C73	6247(9)	357(6)	338(9)	120(10)	36(4)	112(10)	20(5)	3(8)	-20(5)
C74	6546(8)	770(6)	2183(8)	94(8)	31(4)	89(8)	9(5)	-6(7)	3(5)
C75	6389(8)	1148(6)	2992(8)	96(8)	40(4)	83(8)	2(5)	-13(7)	13(5)
C76	7908(7)	3275(6)	2404(8)	71(7)	50(5)	79(8)	0(4)	7(6)	-2(5)
C77	7876(9)	3979(7)	2114(9)	96(9)	51(5)	113(10)	-19(5)	21(8)	-9(6)
C78	5127(11)	930(8)	-1905(9)	132(13)	63(6)	103(10)	1(7)	-1(9)	-29(6)
S(SCN)	1006(8)	1567(6)	1333(6)	227(8)	165(6)	245(8)	-99(6)	-21(6)	19(6)
C(SCN)	9149(9)	1662(8)	1696(11)	65(9)	83(8)	153(14)	-2(6)	13(8)	-14(8)
N(SCN)	8736(12)	1348(7)	1475(13)	207(15)	58(6)	289(21)	35(8)	14(14)	15(9)
CS	4551(0)	2675(0)	1432(0)	59(0)	40(0)	70(0)	3(0)	2(0)	0(0)

(b) Ca⁺-nonactin complex

C(1)	3670(4)	-1464(8)	1260(5)	42(3)	147(11)	66(4)	17(5)	14(3)	20(6)
C(2)	31(4)	-2049(8)	447(5)	41(4)	152(11)	58(4)	-1(5)	3(3)	4(6)
C(3)	2205(4)	-1744(8)	534(5)	44(3)	129(11)	73(5)	-3(5)	11(3)	4(6)
O(4)	2093(3)	-344(5)	565(3)	43(2)	146(7)	74(3)	0(3)	-13(2)	-12(4)
C(5)	1276(4)	55(8)	88(5)	44(4)	154(12)	74(5)	7(5)	-6(3)	-22(6)
C(6)	1407(4)	1021(9)	-681(5)	51(4)	206(13)	59(4)	22(7)	-12(3)	-7(7)
C(7)	1772(5)	2288(9)	-347(5)	58(4)	193(14)	61(5)	0(6)	-2(3)	-1(7)
O(8)	1141(3)	2882(6)	201(3)	53(3)	182(8)	66(3)	1(4)	-16(2)	-13(4)
C(9)	1398(5)	3435(8)	1033(5)	54(4)	138(11)	62(4)	-19(5)	-5(3)	23(6)
C(10)	686(4)	3967(9)	1501(5)	45(3)	146(11)	80(5)	-3(6)	-13(3)	1(7)
C(11)	808(5)	3710(8)	2546(5)	57(4)	146(13)	66(5)	-7(5)	5(3)	-4(6)
O(12)	737(3)	2307(5)	2700(3)	60(3)	142(8)	68(3)	-1(4)	26(2)	10(4)
C(13)	541(5)	2124(9)	3635(5)	67(4)	205(14)	58(4)	-2(6)	14(4)	0(7)
C(14)	-155(4)	1096(9)	3607(5)	49(4)	204(14)	58(4)	11(6)	12(3)	27(7)
C(15)	40(5)	-243(9)	3316(5)	57(4)	211(14)	45(4)	8(6)	-3(3)	16(6)
O(16)	711(3)	-763(6)	4008(3)	53(2)	199(8)	45(2)	18(4)	1(2)	12(4)
O(17)	3563(3)	-1629(7)	2060(3)	64(3)	316(12)	55(3)	-27(5)	7(2)	26(5)
C(18)	3260(6)	-3504(10)	409(7)	67(5)	193(15)	128(8)	14(7)	7(5)	-27(9)
C(19)	1609(5)	-2197(9)	-294(6)	48(4)	170(13)	84(5)	-22(6)	0(4)	-3(7)
C(20)	189(5)	-1297(9)	-230(6)	53(4)	196(15)	116(7)	-10(6)	-27(4)	-13(8)
C(21)	1942(6)	3238(11)	-1110(7)	89(6)	275(19)	100(7)	-25(9)	6(5)	42(10)
O(22)	2106(3)	3472(7)	1326(3)	44(2)	365(13)	44(3)	-24(5)	-7(2)	-10(5)
C(23)	607(6)	5449(10)	1311(6)	97(6)	185(15)	96(7)	10(8)	-7(5)	1(8)
C(24)	156(6)	4306(9)	3105(6)	83(5)	169(15)	108(7)	11(7)	15(5)	-33(8)
C(25)	300(7)	3444(10)	3994(7)	132(8)	187(15)	99(7)	-16(9)	51(6)	-21(8)
C(26)	-677(5)	-1208(10)	3302(6)	70(5)	240(17)	79(5)	-31(8)	-11(4)	21(8)
CS	2500(0)	92(0)	2500(0)	58(0)	190(0)	53(0)	0(0)	3(0)	0(0)
S(SCN)	7500(0)	3543(5)	2500(0)	161(4)	288(9)	113(3)	0(0)	39(3)	0(0)
C(SCN)	7500(0)	1962(14)	2500(0)	76(7)	212(21)	78(8)	0(0)	11(6)	0(0)
N(SCN)	7500(0)	865(13)	2500(0)	77(6)	257(19)	97(7)	0(0)	13(5)	0(0)

Table 3. Bond distances (Å) and angles (°), and internal rotation angles (°)

	Cs ⁺ -TNC	Cs ⁺ -NNC		Cs ⁺ -TNC	Cs ⁺ -NNC
C=O			-C-C-		
1-17	1.210 (1.208)	1.196	1-2	1.506 (1.519)	1.516
9-22	1.204 (1.198)	1.172	2-3	1.522 (1.496)	1.511
Mean	1.205	1.184	2-18	1.513 (1.526)	1.494
			3-19	1.494 (1.511)	1.521
			5-6	1.507 (1.523)	1.497
3-4	1.462 (1.452)	1.430	5-20	1.541 (1.517)	1.555
4-5	1.451 (1.460)	1.473	6-7	1.529 (1.532)	1.489
7-8	1.471 (1.478)	1.477	7-21	1.537 (1.545)	1.508
11-12	1.443 (1.444)	1.420	9-10	1.483 (1.504)	1.498
13-12	1.468 (1.454)	1.454	10-11	1.518 (1.503)	1.525
15-16	1.469 (1.469)	1.485	10-23	1.530 (1.558)	1.508
Mean	1.460	1.457	11-24	1.496 (1.523)	1.514
			13-14	1.525 (1.456)	1.526
			13-25	1.534 (1.535)	1.498
9-8	1.343 (1.334)	1.348	14-15	1.507 (1.543)	1.464
1-16	1.325 (1.318)	1.314	15-26	1.499 (1.489)	1.509
Mean	1.330	1.331	19-20	1.544 (1.541)	1.484
			24-25	1.531 (1.504)	1.547
			21-28	1.513 (1.488)	—
			26-27	1.502 (1.508)	—
			Mean		
			C(sp ²)-C(sp ³)	1.503	1.507
			C(sp ³)-C(sp ³)	1.518	1.509

ternal rotation angles about the ester linkages in the 32-membered ring (C6-C7-O8-C9 and its chemically equivalent angles). The Cs⁺ complexes have the largest internal rotation angles (Table 5).

Examination of the molecular structure of Cs⁺-NNC indicated that the C(7)-H1(C7) bond pointed more closely to the central cation than in K⁺-NNC and Na⁺-NNC, as was suggested by Prestegard & Chan (1970). As is also shown in Table 5, the H1(C7) proton is located in close proximity to Cs⁺, under the shielding effect of the cation. In addition, this proton is also in the neighbourhood of the carbonyl O(22) atom and experiences the diamagnetic anisotropic shielding effect of the carbonyl groups, which are strongly polarized in the Cs⁺ complex (Ueno, Kyogoku & Nawata, 1975). Under such circumstances H1(C7) of Cs⁺-NNC may experience a smaller deshielding effect than in the other M⁺-NNC complexes, as was observed in the proton NMR spectra (Prestegard & Chan, 1970). A similar propensity has been observed for Cs⁺-TNC (Ueno *et al.*, 1975).

In the far-IR spectra of Cs⁺-NNC (in absolute CHCl₃) the characteristic absorption bands of ν(M⁺...O) were observed at 142 and 102 cm⁻¹, and for K⁺-NNC at 150 cm⁻¹ (Ivanov *et al.*, 1973). As is shown in Table 4, all the M⁺...O distances in Cs⁺-NNC are approximately equal, and there is no significant difference in the geometry of coordination around the central cation between K⁺-NNC and Cs⁺-NNC. Accordingly, it is probable that two different states of coordination to Cs⁺ may be present in the solution.

Table 3 (cont.)

	Cs ⁺ -TNC	Cs ⁺ -NNC
C(2)-C(1)-O(66)	112.1 (113.1)	112.8
C(2)-C(1)-O(17)	124.4 (123.5)	123.8
O(66)-C(1)-O(17)	123.4 (123.4)	123.4
C(1)-C(2)-C(3)	110.7 (110.4)	110.6
C(1)-C(2)-C(18)	108.1 (107.0)	109.4
C(3)-C(2)-C(18)	111.1 (112.4)	111.2
C(2)-C(3)-O(4)	107.3 (107.7)	109.4
C(2)-C(3)-C(19)	116.4 (117.2)	114.1
O(4)-C(3)-C(19)	105.2 (104.4)	104.6
C(3)-O(4)-C(5)	109.3 (110.2)	111.5
O(4)-C(5)-C(6)	111.0 (109.6)	109.4
O(4)-C(5)-C(20)	105.3 (105.3)	102.5
C(6)-C(5)-C(20)	113.1 (109.8)	113.9
C(5)-C(6)-C(7)	112.9 (114.9)	113.7
C(6)-C(7)-O(8)	107.6 (106.5)	105.1
C(6)-C(7)-C(21)	110.8 (112.7)	114.7
O(8)-C(7)-C(21)	107.5 (107.3)	108.6
C(7)-O(8)-C(9)	119.1 (119.0)	118.8
C(3)-C(19)-C(20)	101.0 (101.5)	102.4
C(5)-C(20)-C(19)	101.9 (103.9)	105.5
C(28)-C(21)-C(7)	113.9 (112.7)	—
O(8)-C(9)-C(10)	111.8 (111.2)	112.3
O(8)-C(9)-O(22)	121.6 (122.2)	121.9
C(10)-C(9)-O(22)	126.6 (126.6)	125.8
C(9)-C(10)-C(11)	109.9 (109.7)	110.6
C(9)-C(10)-C(23)	108.8 (106.9)	109.7
C(11)-C(10)-C(23)	110.4 (110.9)	111.1
C(10)-C(11)-O(12)	107.0 (107.9)	109.4
C(10)-C(11)-C(24)	116.3 (115.6)	115.4
O(12)-C(11)-C(24)	104.8 (105.1)	105.8
C(11)-O(12)-C(13)	108.8 (109.5)	107.5
O(12)-C(13)-C(14)	108.8 (109.4)	109.6
O(12)-C(13)-C(25)	106.5 (105.0)	107.2
C(14)-C(13)-C(25)	113.4 (114.5)	113.7
C(13)-C(14)-C(15)	115.3 (116.2)	117.4
C(14)-C(15)-O(16)	106.0 (105.9)	107.4

Table 3 (cont.)

	Cs ⁺ -TNC	Cs ⁺ -NNC
C(14)-C(15)-C(26)	112.8 (114.3)	114.6
O(16)-C(15)-C(26)	109.3 (108.3)	106.2
C(51)-O(16)-C(15)	120.3 (119.3)	120.8
C(11)-C(24)-C(25)	103.2 (101.1)	99.5
C(13)-C(25)-C(24)	101.2 (103.4)	103.8
C(27)-C(26)-C(15)	114.1 (114.3)	—
Internal rotation angles		
32-membered ring		
C(65)-O(66)-C(1)-C(2)	-177.9 (-179.2)	-172.6
O(66)-C(1)-C(2)-C(3)	-139.9 (-142.2)	-129.3
C(1)-C(2)-C(3)-O(4)	62.7 (65.8)	58.5
C(2)-C(3)-O(4)-C(5)	146.7 (149.7)	144.9
C(3)-O(4)-C(5)-C(6)	-118.6 (-119.3)	-121.7
O(4)-C(5)-C(6)-C(7)	-57.6 (-59.9)	-66.4
C(5)-C(6)-C(7)-O(8)	-66.1 (-64.5)	-63.2
C(6)-C(7)-O(8)-C(9)	130.8 (129.4)	135.1
C(7)-O(8)-C(9)-C(10)	174.9 (174.3)	-179.8
O(8)-C(9)-C(10)-C(11)	145.2 (145.8)	140.1
C(9)-C(10)-C(11)-O(12)	-64.9 (-66.0)	-65.0
C(10)-C(11)-O(12)-C(13)	-147.3 (-144.7)	-156.3
C(11)-O(12)-C(13)-C(14)	121.8 (119.6)	132.5
O(12)-C(13)-C(14)-C(15)	64.5 (62.8)	63.4
C(13)-C(14)-C(15)-O(16)	63.0 (64.1)	62.5
C(14)-C(15)-O(16)-C(51)	-130.5 (-131.0)	-139.7
Ester		
O(17)-C(1)-O(66)-C(65)	0.7 (1.2)	6.8
O(17)-C(1)-C(2)-C(3)	41.6 (37.4)	51.3
O(17)-C(1)-C(2)-C(18)	-80.3 (-85.2)	-71.6
O(22)-C(9)-O(8)-C(7)	-2.9 (-4.4)	1.0
O(22)-C(9)-C(10)-C(11)	-37.2 (-35.5)	-40.7
O(22)-C(9)-C(10)-C(23)	83.8 (84.9)	82.2
Methyl		
C(18)-C(2)-C(1)-O(66)	98.3 (95.2)	107.9
C(18)-C(2)-C(3)-O(4)	-177.2 (-174.7)	-179.8
C(18)-C(2)-C(3)-C(19)	-59.8 (-57.6)	-63.0
C(23)-C(10)-C(9)-O(8)	-93.8 (-93.8)	-97.0
C(23)-C(10)-C(11)-O(12)	175.2 (176.1)	172.9
C(23)-C(10)-C(11)-C(24)	58.5 (58.8)	53.8
Ethyl		
C(21)-C(7)-C(6)-C(5)	176.7 (178.1)	177.7
C(21)-C(7)-O(8)-C(9)	-109.7 (-109.7)	-101.7
C(28)-C(21)-C(7)-C(6)	177.8 (-180.0)	—
C(28)-C(21)-C(7)-O(8)	60.5 (63.3)	—
C(26)-C(15)-C(14)-C(13)	-177.4 (-176.7)	-179.8
C(26)-C(15)-C(16)-C(51)	107.7 (106.0)	97.3
C(27)-C(26)-C(15)-C(14)	-179.4 (-179.7)	—
C(27)-C(26)-C(15)-O(16)	-61.7 (-61.9)	—
THF ring		
C(19)-C(3)-O(4)-C(5)	22.1 (24.5)	22.2
C(3)-O(4)-C(5)-C(20)	4.2 (-1.3)	-0.5
O(4)-C(5)-C(20)-C(19)	-27.6 (-22.0)	-22.1
C(5)-C(20)-C(19)-C(3)	40.0 (36.0)	35.0
C(20)-C(19)-C(3)-O(4)	-38.5 (-36.8)	-35.2
C(24)-C(11)-O(12)-C(13)	-23.3 (-20.8)	-31.5
C(11)-O(12)-C(13)-C(25)	-0.8 (-3.7)	8.6
O(12)-C(13)-C(25)-C(24)	23.6 (26.9)	16.8
C(13)-C(25)-C(24)-C(11)	-37.2 (-38.4)	-33.7
C(25)-C(24)-C(11)-O(12)	38.0 (36.9)	40.2

(b) Structural differences in the alkali-metal complexes of tetranactin and nonactin

The difference in the conformational energy (sum of U_{NB} , U_{TOR} , U_{EL} and U_{ID}) between the Na⁺ and the Cs⁺ complexes of tetranactin and nonactin (Table 6) as cal-

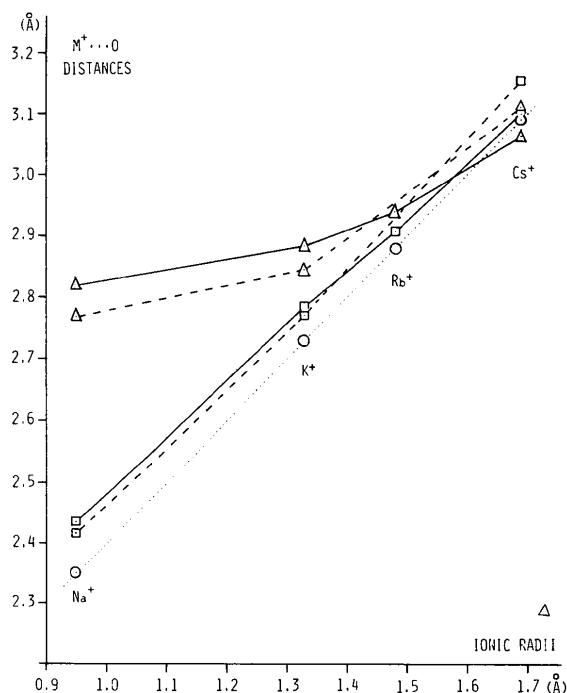


Fig. 2. Distances between the central cation and the ligand oxygen atom. Observed values for the tetranactin complexes (solid lines) and those for the nonactin complexes (broken lines) are plotted against the ionic radii of the cations (abscissa). Δ Distance between the cation and the ether oxygen atom. \square Distance between the cation and the carbonyl oxygen atom. \circ Sum of the ionic radius of the central cation and the van der Waals radius of the oxygen atom ($M^+ + O$ distance).

Table 4. Coordination geometry around Cs⁺

The bond distances (Å) between Cs⁺ and the ligand O atoms, and the angles (°) between the directions of the bond and the lone-pair orbitals of the O atoms are listed.

	Cs ⁺ -TNC			Cs ⁺ -NNC		
Ether						
O(4)	3.087	9.6	100.1	3.069	10.8	96.4
O(12)	3.097	8.8	101.4	3.163	4.0	107.7
O(54)	3.037	4.8	104.0	—	—	—
O(62)	3.031	12.2	97.1	—	—	—
Mean	3.063	8.9	100.7	3.116	7.4	102.1
Carbonyl						
O(17)	3.057	79.9	82.7	3.181	63.0	87.7
O(22)	3.073	79.2	83.1	3.133	80.7	82.0
O(67)	3.113	79.5	81.5	—	—	—
O(72)	3.163	79.5	84.1	—	—	—
Mean	3.101	79.5	82.9	3.157	71.9	84.9

culated by the procedure described in the preceding paper (Sakamaki, Iitaka & Nawata, 1976) indicates that the difference in conformational energy between Cs^+-NNC and Na^+-NNC is larger than that between Cs^+-TNC and Na^+-TNC , and the difference in the internal rotation angles about the ester linkage between Cs^+-NNC and Na^+-NNC is also larger than that between the corresponding tetranactin complexes (Table 5). In addition, the largest distortion in the arrangement of the ligand O atom was observed in Cs^+-NNC (Table 7).

These facts suggest that the nonactin molecule is more deformable than tetranactin. The deformation of the tetranactin molecule seems to be hindered by the substituent groups (ethyl groups) which make the expansion of the inner cavity of the molecule difficult and this results in shorter $\text{Cs}^+\cdots\text{O}(\text{ether})$ distances than in the nonactin complex. As is shown in Fig. 2, the $\text{Cs}^+\cdots\text{O}(\text{ether})$ distance in the tetranactin complex is slightly shorter than the $\text{Cs}^+ + \text{O}$ distance indicating that the cavity of the tetranactin molecule reaches almost its maximum size in Cs^+-TNC .

The above mentioned structural features may be responsible for the $\text{Na}^+ > \text{Cs}^+$ selectivity in tetranactin and $\text{Cs}^+ > \text{Na}^+$ selectivity in nonactin, which were observed in the 'salt extraction' and 'lipid bilayers' experiments (Eisenman *et al.*, 1975). For smaller ions such as Li^+ (ionic radius = 0.60 Å) the accommodation of ions into the cavity may be difficult, because the ether O atoms are not able to come close enough to hold the ions (Fig. 2) and the stronger hydration energy of Li^+ ($-120.3 \text{ kcal mol}^{-1}$) may also prevent formation of a stable complex molecule. It is to be noted that no salt-induced shift of the signals has been observed in the proton NMR spectra of tetranactin in acetone- d_6 solution containing an approximately equal molar amount of LiSCN (Nawata, 1976).

(c) Crystal structure

As described previously (Sakamaki *et al.*, 1976), the arrangement of the ions in the form I crystal of the

tetranactin complexes ($P2_1/n$) is a distorted NaCl type in which SCN^- ions can be regarded as spheres because of the disorder in the crystal. In Cs^+-TNC , which crystallizes in form I, intermolecular short contacts are approximately equal to those in the other complexes of the same crystal form (Table 8).

In the crystal of Cs^+-NNC , both Cs^+ and SCN^- ions are located on the twofold axes (Fig. 3) and no signs of disorder were observed for SCN^- . Interatomic distances in the SCN^- ion for N—C and C—S bonds are 1.090 (± 0.019) and 1.601 (± 0.015) Å, respectively,

Table 6. Conformational energy (kcal mol^{-1})

U_{NB} = non-bonded interaction energy by the Lennard-Jones 6-12 potential function. U_{TOR} = torsional energy. U_{EL} = Coulomb force. U_{ID} = ion-dipole interaction. Positional parameters of H atoms, included in the calculation, were estimated stereochemically.

	U_{NB}	U_{TOR}	U_{EL}	U_{ID}
Cs^+-TNC	-77.01	26.06	3.14	-45.80
Na^+-TNC	-83.07	26.00	10.45	-79.42
Cs^+-NNC	-66.36	27.11	2.64	-41.65
Na^+-NNC	-76.52	24.73	10.63	-80.41

Table 7. Distortion from the cubic arrangement of ligand O atoms

R.m.s. deviations of 12 O...O edge lengths, 12 O...O face-diagonal lengths and 24 O...O...O edge angles are given in parentheses.

	Mean edge length (O...O) (Å)	Mean face-diagonal length (O...O) (Å)	Mean edge angle (O...O...O) (°)
Cs^+-TNC	3.60 (0.33)	5.00 (0.51)	88.2 (11.0)
Rb^+-TNC^1	3.42 (0.22)	4.75 (0.46)	90.0 (10.2)
$\text{K}^+-\text{TNC}(\text{I})^1$	3.30 (0.17)	4.61 (0.38)	88.8 (9.1)
Na^+-TNC^1	3.08 (0.10)	4.28 (0.43)	88.8 (11.4)
Cs^+-NNC	3.73 (0.34)	4.95 (0.85)	86.1 (15.6)
K^+-NNC^2	3.27 (0.11)	4.56 (0.33)	89.2 (7.0)
Na^+-NNC^3	3.02 (0.08)	4.22 (0.40)	89.3 (9.3)

References: (1) Sakamaki, Iitaka & Nawata (1976). (2) Dobler, Dunitz & Kilbourn (1969). (3) Dobler & Phizackerley (1974).

Table 5. Stereochemistry about the methine proton H1(C7)

The averaged values are listed, assuming the molecular structures of the complexes to have $S_4(\bar{4})$ symmetry. Positional parameters of H1(C7) were estimated stereochemically. TNC(I) represents the form I crystal of the tetranactin complex.

	Distance (Å) $\text{M}^+\cdots\text{H1}(\text{C7})$	Angle (°) $\text{M}^+-\text{C}(\text{7})-\text{H1}(\text{C7})$	Eclipse angle (°)	Internal rotation	Distance (Å) $\text{O}(\text{22})\cdots\text{H1}(\text{C7})$
			between the $\text{C}(\text{9})=\text{O}(\text{22})$ and $\text{C}(\text{7})-\text{H1}(\text{C7})$ bonds	angle about the $\text{C}(\text{6})-\text{C}(\text{7})-\text{O}(\text{8})-\text{C}(\text{9})$ bonds	
Cs^+-TNC	3.876	48.6	12.5	130.4	2.290
Na^+-TNC^1	3.870	50.5	12.3	112.1	2.273
$\text{K}^+-\text{TNC}(\text{I})^1$	3.930	51.1	8.6	121.1	2.269
Cs^+-NNC	3.727	46.0	17.1	137.4	2.338
Na^+-NNC^2	3.945	54.9	16.6	105.3	2.318
K^+-NNC^3	3.968	54.0	9.5	115.9	2.257

References: (1) Sakamaki, Iitaka & Nawata (1976). (2) Dobler & Phizackerley (1974). (3) Dobler, Dunitz & Kilbourn (1969).

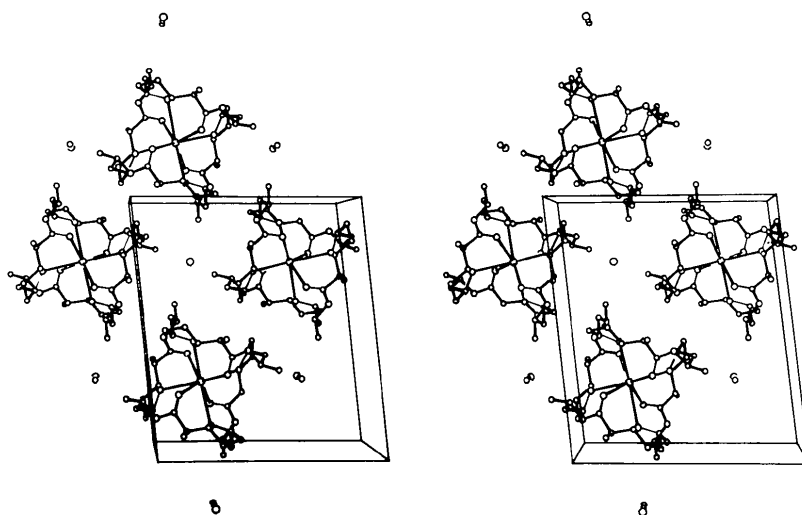


Fig. 3. Stereoscopic view of the crystal structure of the Cs⁺-nonactin complex along [010], by the plotting program *ORTEP* (Johnson, 1965).

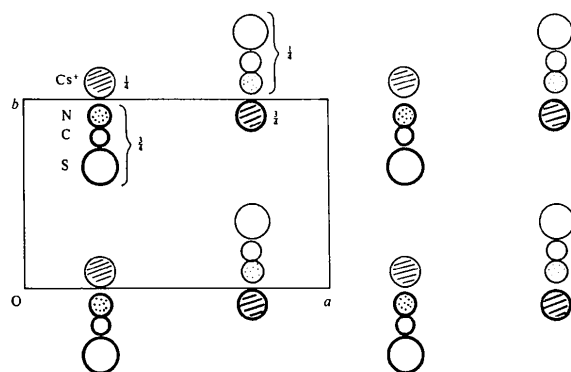


Fig. 4. Arrangement of the ions in the crystal of the Cs⁺-nonactin complex viewed along [001].

which are slightly shorter than those observed in the crystal structure of KSCN (N-C = 1.149 ± 0.014, C-S = 1.689 ± 0.013 Å) (Akers, Peterson & Willett, 1968). A perspective view of the crystal structure of Cs⁺-NNC drawn by the *ORTEP* program (Johnson, 1965) is shown in Fig. 3. Fig. 4 is a schematic view of the crystal structure showing the arrangement of Cs⁺ and SCN⁻ ions in the crystal. Boldly assuming the ions to be spheres, this structure type can be described as a distorted tetragonal PbO structure in which the O atoms are replaced by the complexed cations and the Pb atoms by SCN⁻ ions. This is a new structure type to be found in the metal-ion complexes of nactins. Intermolecular interatomic distances less than 3.8 Å in both Cs⁺ complexes are tabulated in Table 8.

Table 8. Short contacts (Å) of less than 3.8 Å

Cs ⁺ -TNC		Cs ⁺ -NNC	
O(8 ^l)...C(70 ^{ll})	3.702	C(23 ^l)...C(19 ^{ll})	3.797
C(14 ^l)...O(66 ^{ll})	3.736	C(5 ^l)...C(20 ^{ll})	3.728
O(16 ^l)...C(64 ^{ll})	3.631	O(8 ^l)...C(20 ^{ll})	3.650
O(16 ^l)...C(75 ^{ll})	3.622	C(14 ^l)...O(16 ^{lv})	3.657
C(25 ^l)...O(66 ^{ll})	3.557		
C(70 ^l)...O(8 ^{lv})	3.702		
C(24 ^l)...C(73 ^v)	3.757		
C(18 ^l)...N(SCN ^{vl})	3.497		

Symmetry codes

(i)	x, y, z	(i)	x, y, z
(ii)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	(ii)	$x, 1 + y, z$
(iii)	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$	(iii)	$-x, -y, -z$
(iv)	$\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$	(iv)	$-x, -y, 1 - z$
(v)	$1 - x, -y, -z$		
(vi)	$1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		

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References

- AKERS, C., PETERSON, S. W. & WILLETT, R. D. (1968). *Acta Cryst.* **B24**, 1125-1126.
 DOBLER, M., DUNITZ, J. D. & KILBOURN, B. T. (1969). *Helv. Chim. Acta*, **52**, 2573-2583.
 DOBLER, M. & PHIZACKERLEY, R. P. (1974). *Helv. Chim. Acta*, **57**, 664-674.
 EISENMAN, G., KRASNE, S. & CIANI, S. (1975). *Ann. NY Acad. Sci.* **264**, 34-60.

- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- IVANOV, V. T., KOGAN, G. A., TULCHINSKY, V. M., MIROSHNIKOV, A. V., MIKHALYOVA, I. I., EVSTRATOV, A. V., ZENKIN, A. A., KOSTESKY, P. V. & OVCHINNIKOV, YU. A. (1973). *FEBS Lett.* **30**, 199–204.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- NAWATA, Y. (1976). Unpublished work.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- PIODA, L. A. R., WACHTER, H. A., DOHNER, R. E. & SIMON, W. (1967). *Helv. Chim. Acta*, **50**, 1373–1376.
- PRESTEGARD, J. H. & CHAN, S. I. (1970). *J. Amer. Chem. Soc.* **92**, 4440–4446.
- SAKAMAKI, T., IITAKA, Y. & NAWATA, Y. (1976). *Acta Cryst.* **B32**, 768–774.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- UENO, M., KYOGOKU, Y. & NAWATA, Y. (1975). The 2nd Symposium on Molecular Structure of Biologically Related Substances, Tokyo, Japan.

Acta Cryst. (1977). **B33**, 59–69

X-ray Determination of the Electron Distribution in Crystals of $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ at 80 K

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X-ray diffraction data for a hexaamminecobalt(III) hexacyanochromate(III) single crystal were collected at 80 K. The crystal is isomorphous with $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$: space group $R\bar{3}$; $a_r = 7.372(4) \text{ \AA}$, $\alpha = 97.93(3)^\circ$; $Z = 1$. The atom valence-scattering factors were refined to determine the electron populations and atomic parameters. The aspherical charge refinement shows that the valence-electron distributions of Co and Cr atoms outside the Ar core are related to the trigonal distortion of the complex ions. It also elucidates the difference between the bonding character of the metal–CN and metal–NH₃ bonds. The charges on Co and Cr are found to be largely neutralized. In addition, the net charges on an NH₃ molecule and a CN group are determined to be about +0.5 and –0.7 e respectively. Consequently, in agreement with the traditional chemical picture, $[\text{Co}(\text{NH}_3)_6]$ and $[\text{Cr}(\text{CN})_6]$ have charges of +3 and –3 e respectively. The same conclusion is drawn from a similar analysis of the room-temperature data for a $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ crystal; the charge on NH₃ is again +0.5, but on a CN group in $[\text{Co}(\text{CN})_6]^{3-}$ the charge is –0.3 e.

Introduction

In recent years a number of molecular crystals, as well as simple crystals of high symmetry such as NaCl and diamond, have been investigated to determine electron distributions in solids by means of X-ray diffraction and/or neutron diffraction (Coppens, 1975). In many of their residual density maps, excess electrons are clearly observed in bond and lone-pair regions.

As for metallo-organic crystals, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (hereafter abbreviated as $[\text{Co}][\text{Co}]$) was the first to be studied (Iwata & Saito, 1973). In the final residual density maps of this complex, an aspherical charge distribution around transition-metal atoms was found. In addition, excess electrons were observed in metal–ligand and C–N

bond regions. Since then, several types of metal complexes have been examined in order to observe the aspherical distribution of electrons by difference syntheses (for example, $\gamma\text{-Ni}_2\text{SiO}_4$: Marumo, Isobe, Saito, Yagi & Akimoto, 1974; $\gamma\text{-Fe}_2\text{SiO}_4$: Marumo & Isobe, 1974; Marumo & Saito, 1974; $\gamma\text{-Co}_2\text{SiO}_4$: Marumo, Isobe & Akimoto, 1975; TiO_2 : Shintani, Sato & Saito, 1975; an Rh complex: Miyamae, Sato & Saito, unpublished; a low-symmetry Co complex: Maslen, Ridout & White, 1975; a Ti complex: Manohar & Schwarzenbach, 1974). The direct observation of asphericity in electron distributions in metal complexes enables us to understand the physical and chemical nature of metal–ligand bonds, and of transition-metal complexes themselves.

Although the X-ray diffraction study of the title compound $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ (hereafter abbreviated as $[\text{Co}][\text{Cr}]$) was previously carried out at room

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