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A Powder Neutron Diffraction Study of the Room Temperature Structure of $Cs_2LiCr(CN)_6$

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The room temperature structure of $Cs_2LiCr(CN)_6$ has been determined by profile analysis of neutron powder diffraction data. Unlike the Mn, Fe and Co compounds of the first-row transition-metal hexacyanides $Cs_2LiM(CN)_6$ (M = Cr, Mn, Fe, Co), all of which crystallize in the cubic space group *Fm*3*m*, the Cr compound crystallizes in a tetragonal structure. The tetragonal distortion of the unit cell has been confirmed by X-ray powder diffraction. The space group assigned is *P*4/*mnc* with the cell parameters $a_T = 7{\cdot}600\ (1)$, $c = 10{\cdot}777\ (2)$ Å and $Z = 2$. The final least-squares refinement gave a weighted profile residual of 10·4% for 670 data points and 26 least-squares parameters. This value was achieved with anisotropic temperature parameters for C and N atoms. The compound is known to undergo a structural phase transition to the cubic space group *Fm*3*m* at ~350 K. The room temperature structure is related to the high temperature phase by rotations of the $Cr(CN)_6$ octahedra about the tetragonal *c* axis such that the octahedra on alternate layers perpendicular to the *c* axis rotate in opposite directions. The C octahedron about the Cr atom is rotated by 4·9° and the N octahedron about the Li atom is rotated by 9·8° relative to their cubic phase positions; both octahedra exhibit substantial tetragonal distortions.

Introduction

Extensive studies of the structure of hexacyano complexes of the first-row transition metals have been carried out with a view primarily to characterizing the metal–ligand bonding. Structural studies provide accurate M–ligand (M = Cr, Mn, Fe, Co) and C–N bond lengths, the systematic variation of which in an isostructural series can be correlated with M–CN σ and π bonding trends (Swanson & Ryan, 1973). The tripotassium salts $K_3M(CN)_6$ have been the subject of experimental investigations for quite some time (Gottfried & Nagelschmidt, 1930). Although the series is known to be isostructural (Gupta, Milledge & McCarthy, 1974), polytypism (Kohn & Townes, 1961) and order–disorder structures (Jagner, Ljungström & Vannerberg, 1974) are prevalent. These factors together with the low site symmetry of the $M(CN)_6$ groups significantly detract from the usefulness of the M–ligand distances in the $K_3M(CN)_6$ series as a test of any bonding model. However, the recent synthesis of the cubic $Cs_2LiCo(CN)_6$, belonging to the highly symmetric space group *Fm*3*m* (Wolberg, 1969), has prompted intensive structural investigations of the series $Cs_2LiM(CN)_6$ (*e.g.* Armstrong, Chadwick, Jones, Sarneski, Wilde & Yerkess, 1973; Swanson & Ryan, 1973; Ryan & Swanson, 1974). One aim of these studies has been to obtain accurate M–C and C–N bond lengths in a highly symmetric, low-spin isostructural series, so that these can be correlated with the variations expected due to the increase in the number of t_{2g} electrons from three to six (Chadwick & Sharpe, 1966; Swanson & Ryan, 1973). In Wolberg's ideal structure type the transition metal and the Li atoms occupy octahedral and the Cs atoms tetrahedral lattice sites.

The objectives of the present study were twofold: first, to probe into the high *R* value (12·2%) obtained for $Cs_2LiCr(CN)_6$ in the *Fm*3*m* structure, based on 76 single-crystal 'face-centred cubic' neutron structure factors; secondly, to investigate the degree of covalency in the nominally ionic Cr^{III}–$(CN)^-$ bonding using polarized neutron scattering techniques at low temperature (Nathans, Alperin, Pickart & Brown, 1963). Here, only the structural part of our study will be discussed. Initial neutron powder data revealed that at 4·2 K the structure of $Cs_2LiCr(CN)_6$ is noncubic and that at room temperature, contrary to previous assumptions, the structure is primitive and so does not belong to the space group *Fm*3*m*. Although the room temperature powder profile could be indexed on the basis of a cubic unit cell having dimensions similar to those of the Co salt, attempts to refine the structure in any likely

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cubic space group did not meet with success. Meanwhile, based on a single-crystal X-ray study Swanson & Ryan (1973) reported that while the Mn, Fe and Co salts are indeed cubic (*Fm*3*m*) at room temperature, the Cr salt has a tetragonal room temperature structure. In a later study Ryan & Swanson (1974) confirmed the tetragonal cell at room temperature. From the observed systematic absences they suggested $P4_22_12$ as the space group, but they did not succeed in refining the structure. They also reported that the compound undergoes a phase transformation at ~ 350 K to the cubic space group *Fm*3*m*, thereby becoming isostructural with the room temperature structure of the rest of the series $Cs_2LiM(CN)_6$.

Neutron diffraction provides a very sensitive tool for the determination of C and N atom positions in heavy-metal cyano complexes, because not only are the scattering amplitudes of these two atoms by far the largest in the molecular unit, they are also considerably different from each other. This is very important when the major difference between two structural phases lies in a small shift in the relative positions of the C and N atoms. The X-ray scattering amplitude of Cs relative to Li is so large (55 : 3) as to render the diffraction data insensitive to Li positions; for neutrons the situation is considerably better, the neutron scattering amplitudes $|a|$ of Cs and Li being in the ratio 55:21. In the present case, therefore, it would appear that neutrons have distinct advantages over X-rays.

Recent developments in the analysis of neutron powder profiles have made it possible to investigate quite a number of complex structures. In cases where either a good untwinned single crystal or a large enough single crystal suitable for neutron diffraction experiments cannot be found, the profile-analysis technique can be especially suitable (Von Dreele, Eyring, Bowman & Yarnell, 1975). While refining the structure of $Sr_2Fe_2O_5$ (Greaves, Jacobson, Tofield & Fender, 1975) it has been shown that not only is this technique suitable for refining structural parameters but, in favourable cases, it makes it possible to decide between alternative space groups, which would in general require single-crystal analysis.

Neutron diffraction measurements

Neutron diffraction data were collected on a powder sample of $Cs_2LiCr(CN)_6$ at room temperature using the diffractometer PANDA on the PLUTO reactor at AERE, Harwell. The sample was contained in a thin-walled vanadium can of cylindrical shape. The incident wavelength used was 1·543 Å, and was obtained by reflexion from the (511) plane of a germanium monochromator with a take-off angle ($2\theta_m$) of 90·0°. The data were recorded over the angular range $8{\cdot}0° \leq 2\theta \leq 90{\cdot}0°$ in steps of 0·1°, the counting time for each data point being determined by an incident beam fission counter monitor. No absorption or extinction correction was made.

Structure determination and refinement

The structural parameters and the lattice parameters were refined by full-matrix least-squares analysis of the powder profile using a modified version of the program originally due to Rietveld (Rietveld, 1967; Hewat, 1973). Initial efforts to refine the structure by least-squares analysis of integrated peak intensities of apparently resolvable peaks did not produce satisfactory results. The profile-analysis technique makes full use of the information available in the diffraction pattern including overlapping peaks, which become a common feature of the pattern at high angles.

The intensity at each point (2θ value) is calculated by summing contributions of all the Bragg reflexions which overlap at that point. The program minimizes the weighted difference between the observed and calculated profile and gives the profile residual:

$$R_p = \sum\left|y(\text{obs}) - \frac{1}{c}y(\text{calc})\right| \Big/ \sum\left|y(\text{obs})\right|$$

and the weighted residual:

$$R_{pw} = \left\{\sum w\left[y(\text{obs}) - \frac{1}{c}\,y(\text{calc})\right]^2 \Big/ \Sigma\, w[y(\text{obs})]^2\right\}^{1/2}$$

where y(obs), y(calc), w and c are the observed counts, calculated counts, weight assigned to the counts and scale factor respectively. The neutron scattering lengths used in the refinement were: $0{\cdot}55 \times 10^{-14}$ m for Cs, $-0{\cdot}214 \times 10^{-14}$ m for Li, $0{\cdot}352 \times 10^{-14}$ m for Cr, $0{\cdot}665 \times 10^{-14}$ m for C and $0{\cdot}94 \times 10^{-14}$ m for N (Bacon, 1972).

As mentioned earlier, whereas detailed results on the room temperature structure of the Mn, Fe and Co salts are now available, in the case of the Cr salt this is not so. The only definite thing known about the structure is the unit cell.

The X-ray data showed that the tetragonal cell is closely related to the high temperature cubic cell both in intensity and cell constants. The cell parameters in the tetragonal phase, as found by Ryan & Swanson (1974), are $a_T = 7{\cdot}600$ (3), $c = 10{\cdot}778$ (3) Å, and the corresponding parameter a_c in the cubic phase is 10·780 (2) Å. This shows that $a_c \simeq \sqrt{2}a_T \simeq c$ with the $c/(\sqrt{2}a_T)$ ratio 1·0028 (5). The tetragonal distortion of the cell is thus much too small to be observable in the neutron powder pattern in the form of resolvable peaks. As will be shown later, the profile-fitting technique is sensitive enough to respond to such small distortions. The tetragonal distortion is, however, clearly evident in five triplets out to and including $N = 56$ ($N = h^2 + k^2 + l^2$) in the X-ray powder diffraction pattern (see Fig. 1).

In their X-ray study Ryan & Swanson (1974) observed that the 'tetragonal reflexions' (reflexions not consistent with the cubic *Fm*3*m* group) were very weak. This can be understood from the fact that contributions to these reflexions come from a small shift in the C and N positions and X-rays are not a very efficient probe to detect this, especially in the presence of heavy atoms like Cs.

When indexed on the basis of the tetragonal cell, reflexions of the type $h00$: $h = 2n + 1$, $0kl$: $k + l = 2n + 1$ and hhl: $l = 2n + 1$ were found to be absent from the neutron powder data. It should, however, be pointed out that one cannot be certain about the systematic absences in a powder pattern because of the occurrence of overlapping peaks – especially at high angles. This extinction pattern is indicative of the noncentrosymmetric space group *P*4*nc* and the centrosymmetric group *P*4/*mmc*. The possibility of the space group $P4_22_12$, as suggested by Ryan & Swanson (1974), is not ruled out since the extinction pattern observed does include the reflexions forbidden by this space group. The systematic absences consistent with these space groups are:

*P*4*nc*	$0kl$:	$k + l = 2n + 1$
	hhl:	$l = 2n + 1$
*P*4/*mnc*	$0kl$:	$k + l = 2n + 1$
	hhl:	$l = 2n + 1$
$P4_22_12$	$h00$:	$h = 2n + 1$
	$00l$:	$l = 2n + 1$.

The tetragonal coordinate system is related to the cubic coordinate system by a rotation of 45° about the tetragonal *c* axis.

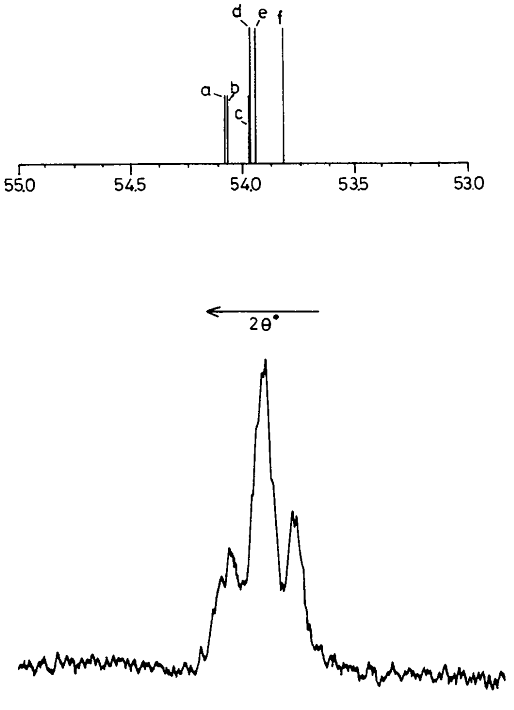

Fig. 1. Assignment of X-ray (Cu *Kα*) powder pattern of $Cs_2LiCr(CN)_6$ ($53{\cdot}0° < 2\theta < 55{\cdot}0°$) at 295 K. The symbols *a*, *b*,...*f* in the figures refer to:

	$hkl(\alpha_i)$	$2\theta_{calc}$*	$2\theta_{obs}$
a	$240(\alpha_2)$	54·122	54·122
b	$332(\alpha_2)$	54·106	
c	$116(\alpha_2)$	53·979	53·978
d	$240(\alpha_1)$	53·976	
e	$332(\alpha_1)$	53·960	
f	$116(\alpha_1)$	53·834	53·834

* With $a = 7{\cdot}591$ and $c = 10{\cdot}764$ Å for $2\theta_{calc}$.

It is reasonable to expect that the atomic positions in the tetragonal phase will be very similar to those in the cubic phase. This is borne out by the fact that the X-ray intensities in the two phases are very closely related. The tetragonal distortion is expected to be mainly due to a rotation (or tilt) of the $Cr(CN)_6$ octahedra. The atomic positions required by symmetry of the space group $P4_22_12$ do not appear to be in keeping with this picture [*i.e.* any reasonable setting of the C and N atoms does not allow any rotation (*International Tables for X-ray Crystallography*, 1952)]. In addition, the observed systematic absences are more restrictive than those required by this space group. The other two space groups, on the other hand, are consistent with the above physical picture (Chowdhury, 1976).

To make sure that reflexions forbidden by the space groups *P*4*nc* and *P*4/*mnc* are not present in the observed diffraction pattern, another set of powder data was collected with a much longer neutron wavelength ($\lambda = 2{\cdot}56$ Å), so that a better resolution could be obtained. This gave well separated diffraction peaks at low angles, but no intensity could be detected at the forbidden reflexion positions.

Refinement of the structure was started with initial positional parameters the same as or very close to those of the high-temperature structure, while the lattice parameters were those as determined from the X-ray data in the room temperature tetragonal phase. Both the space groups, *P*4*nc* and *P*4/*mnc*, were tried. In *P*4/*mnc* the Cs, Li and Cr atoms are in special positions with all three coordinates fixed. In the case of *P*4*nc*, Cs, Li and Cr all have their *z* coordinates general, the *x* and *y* coordinates remaining fixed. With the space group *P*4/*mnc* the structure refined smoothly to final profile residuals $R_p = 10{\cdot}7$ and $R_{pw} = 10{\cdot}4\%$. These values were achieved with anisotropic temperature factors for C and N atoms. The observed and the calculated profile intensities are shown in Fig. 2. Refinement in the other possible space group gave profile residuals not significantly different from these values; also, the final refined atomic positional parameters for Cs, Li and Cr showed no significant shift from the fixed special positions required by the space group *P*4/*mnc*.

We have, therefore, chosen $P4/mnc$ as the space group. The R_p values obtained may be compared with the 'expected' R value, R_{exp} of 7·01%, which is calculated in terms of the number of independent observations, number of least-squares parameters and statistical reliability of the observations. As mentioned by Greaves *et al.* (1975), correct structural models have normally been found to give R_p values such that $R_p \lesssim 2R_{\text{exp}}$. Our results, therefore, point toward the correctness of the model adopted. Indeed, with comparable powder neutron data for previously determined structures, the magnitudes of the R_p values reported by various authors are in most cases very similar to ours, commonly with $R_p \simeq 2R_{\text{exp}}$ (Von Dreele & Cheetham, 1974; Von Dreele *et al.*, 1975; Rietveld, 1969).

Once it became known from the neutron powder pattern that $Cs_2LiCr(CN)_6$ appeared primitive cubic, a set of single-crystal neutron intensities was collected. The data almost certainly relate to a polydomain crystal; thus 75% of the non-face-centred cubic reflexions when transformed to a tetragonal cell have non-integral Miller indices. Nine high-angle, very weak ($I \leq 4\sigma$) reflexions forbidden by the $P4/mnc$ space group were observed out of 90 possible forbidden reflexions. We feel justified in neglecting this small number of forbidden reflexions; they are probably due to double Bragg scattering.

Discussion

The room temperature structure of $Cs_2LiCr(CN)_6$ is tetragonal, unlike the rest of the members of the hexacyano series $Cs_2LiM(CN)_6$, and is very closely related to the high temperature cubic phase. The lattice parameters a_T and c are 7·600 (1) and 10·777 (2) Å respectively, in agreement with the X-ray results. The phase transition from the cubic to the tetragonal structure entails doubling of the primitive unit cell: $V_{\text{cubic}} = \frac{1}{4}(a_c \times a_c \times a_c)$ and $V_{\text{tetragonal}} \simeq (a_c/\sqrt{2} \times a_c/\sqrt{2} \times a_c)$, with $a_c = 10{\cdot}78$ Å. The final refined value of the c/a ratio ($a = \sqrt{2}a_T \simeq a_c$) is 1·0027 (2); this is to be compared with the X-ray value 1·0028 (5). Thus, not only is the c/a ratio, as determined by profile analysis, almost identical with the X-ray results, it also has an accuracy which is comparable with that of the X-ray value. Considering

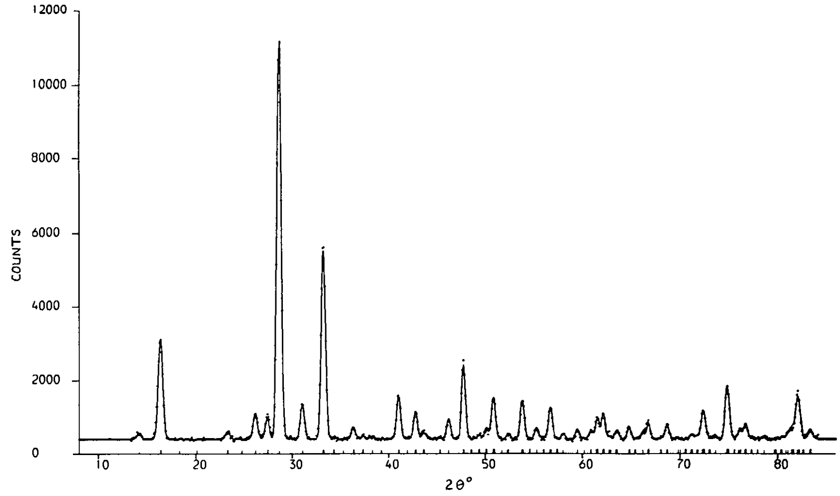

Fig. 2. The observed and calculated diffraction profiles of $Cs_2LiCr(CN)_6$ at 295 K. The dots represent the observed profile and the continuous curve is the calculated profile. Reflexion positions are also shown.

Table 1. *Positional and thermal parameters: space group P4/mnc*

The anisotropic temperature factor has the form: $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ and the isotropic temperature factor is of the form $T = \exp[-B(\sin\theta/\lambda)^2]$, the parameters being in Å².

		x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B
Cr	2(*a*)	0	0	0					1·5 (4)†
Li	2(*b*)	0·5	0·5	0					2·6 (9)†
Cs	4(*d*)	0	0·5	0·25	4·5 (8)	4·5 (8)	4·0 (14)		4·3 (2)
C(1)	8(*h*)	0·168 (1)	0·201 (1)	0	1·0 (5)	0·1 (5)	2·6 (5)	−2·1 (4)	0·8 (2)
C(2)	4(*e*)	0	0	0·206 (1)	4·1 (6)	4·6 (6)	0·9 (8)	—	3·2 (4)
N(1)	8(*h*)	0·247 (1)	0·322 (1)	0	2·4 (4)	7·5 (6)	7·8 (7)	0·6 (4)	6·3 (3)
N(2)	4(*e*)	0	0	0·314 (2)	8·3 (5)	8·3 (5)	1·0 (5)	—	4·8 (3)

† Not independently refined.

that X-ray diffraction, in general, provides a considerably better resolution than neutron powder diffraction, the precision of the result would at first seem surprising. But it is not so, because the profile residual R_p is very sensitive to the positions of the peaks in the profile and hence to any change of lattice parameters. It should, however, be emphasized that whereas the accuracy of the individual values of a_T and c depends on the accuracy of the incident wavelength, that of the c/a ratio does not.

As shown in Table 1, with the exception of the C and N atoms all other atoms retain their respective cubic phase special positions. That the z coordinates of C(1) and N(1) are zero would point to the coplanar nature of the Cr–C(1)–N(1) and Li–N(1)–C(1) bonds. The Cr–C(2)–N(2) and Li–N(2)–C(2) bonds are collinear by symmetry. Fig. 3 shows the projection of the structure on the (001) plane. Although the tetragonal distortion of the unit cell, as determined from the c/a ratio, is quite small, the shifts in the positions of the C and N atoms from their cubic phase positions are quite considerable. Thus the tetragonal distortion of the original cubic structure consists primarily of a rotation of the $Cr(CN)_6$ octahedra about the c axis such that the octahedra on alternate layers perpendicular to the c axis rotate in opposite directions. The C octahedron about the Cr atom rotates by 4·9° and the N octahedron about the Li atom rotates by 9·8° relative to their cubic phase positions. Since only light atoms move in the tetragonal distortion it is easy to see why X-ray data showed close similarity between intensities of reflexions in the cubic and tetragonal phases and why the 'tetragonal reflexions' are weak. The interatomic distances and angles, uncorrected for thermal motions, are shown in Table 2. The tetragonal nature of the distortion is clearly noticeable in the bond lengths. The mean values of the interatomic distances in the room temperature tetragonal phase are quite similar to the corresponding ones in the high temperature cubic phase. The temperature parameters of N and C atoms are highly anisotropic, the components perpendicular to the C–N bond being greater than that along the bond, for the N atoms considerably so. Compared with the rest of the C and N atoms, C(1) shows a low overall thermal motion. The comparable B factors in the cubic phase, as determined by X-rays at 381 K, are: 5·5 (Cs), 3·3 (Li), 1·9 (Cr), 2·6 (C_{min}), 4·4 (C_{max}), 2·4 (N_{min}) and 9·7 (N_{max}). The maximum and minimum values correspond to the components perpendicular to and along the C–N bond directions respectively. One does not expect to make an accurate determination of the individual components of anisotropic temperature parameters from powder diffraction data. The present results would, nevertheless, seem to be broadly in agreement with the X-ray single-crystal measurements, allowing for the lowering of temperature as well as of symmetry.

Owing to the high thermal motions of C(2) and N atoms the interatomic distances and angles computed from the atomic positions obtained from the least-squares refinement need corrections (Busing & Levy, 1964). The need for such corrections is enhanced by

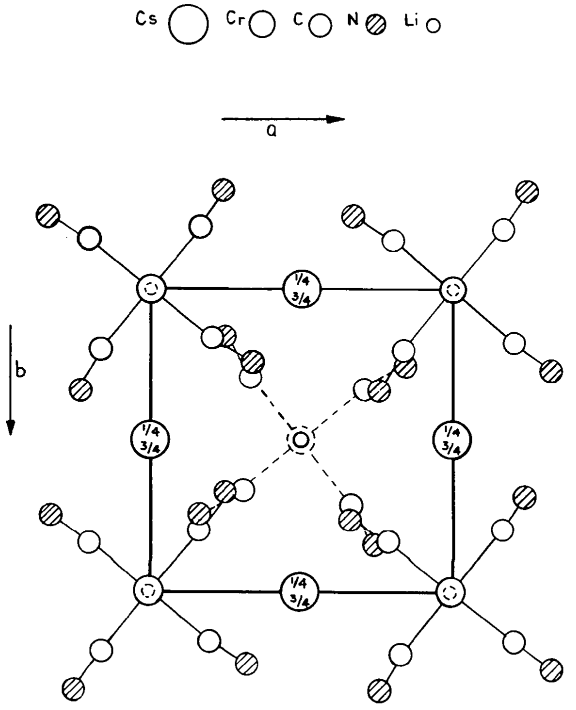

Fig. 3. Projection of the structure on the (001) plane. Carbon and nitrogen atoms along the z axis (fourfold axis) for clarity have not been shown. Continuous lines joining carbon, nitrogen and chromium atoms refer to the $z = 0$ level, while the corresponding broken lines refer to the $z = \frac{1}{2}$ level. Figures indicate the caesium atom z coordinates.

Table 2. *Interatomic distances* (Å) *and angles* (°) (*uncorrected for thermal motion*)

N(2') is related to N(2) by the symmetry operation $\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2}$.

	Present work	Mean value	Cubic phase at $T = 381$ K*
C(1)–N(1)	1·10 (2)	1·13	1·138
C(2)–N(2)	1·16 (2)		
Cr–C(1)	1·99 (1)	2·11	2·046
Cr–C(2)	2·22 (1)		
Li–N(1)	2·35 (1)	2·18	2·206
Li–N(2')	2·01 (1)		
Cs(1)–C(1)	3·75 (1)	3·79	3·866
Cs(1)–C(2)	3·83 (1)		
Cs(1)–N(1)	3·55 (1)	3·70	3·842
Cs(1)–N(2)	3·86 (1)		
Cr–C(1)–N(1)	173·3 (5)		
Li–N(1)–C(1)	158·3 (5)		
Cr–C(1)–Li	171·9 (4)		
Cr–N(1)–Li	162·7 (4)		

* Ryan & Swanson (1974).

the highly anisotropic nature of the C and N atom vibrations. The exact amount of correction is dependent on the model chosen. The apparent C(1)–N(1) and C(2)–N(2) distances, as shown in Table 2, are significantly different. Compared with N(1), C(1) has a low thermal vibration and so the riding model would seem to be a good approximation. When correction based on this model is applied the C(1)–N(1) bond length becomes 1·16 Å (a correction of +0·06 Å). Since the thermal parameters of C(2) are rather similar to those of N(2), the riding model would not provide a good approximation. Nevertheless, when the riding model correction is applied the C(2)–N(2) bond length becomes 1·18 Å (a correction of +0·017 Å). The C(1)–N(1) length is still shorter than the C(2)–N(2) length, but the difference now is much smaller than that calculated from the uncorrected bond lengths. Allowing for the large uncertainties introduced by the thermal vibrations of C and N atoms, the difference between the two C–N bond lengths is not statistically significant. When proper corrections are applied the Li–N distances, especially the Li–N(1) distance, would significantly alter. Similar corrections for thermal motions, however, would not bring about any significant alteration in the Cr–C bond lengths. For example, when corrections based on the riding motion are applied the Cr–C(1) and Cr–C(2) bond lengths become 2·00 and 2·23 Å respectively, compared with the corresponding uncorrected lengths 1·99 and 2·22 Å. Thus the two Cr–C distances are significantly different, indicating the tetragonal nature of the distortion: the $Cr(CN)_6^{3-}$ ion is substantially axially elongated. A measure of the magnitude of this distortion is provided by the recent single-crystal X-ray analysis of $K_3Cr(CN)_6$ (Jagner *et al.*, 1974); here the Cr–C bond lengths are 2·057 (12), 2·075 (7) and 2·100 (10) Å. We are attempting to obtain confirmatory evidence of the 0·23 Å distortion in the Cr–C bond lengths of $Cr(CN)_6^{3-}$ in $Cs_2LiCr(CN)_6$ by refining our single-crystal data in *P*4/*mnc*.

One noticeable feature of the structure is the relatively high, but nearly isotropic, thermal motion of the Cs atoms (r.m.s. vibrational amplitude $\simeq 0{\cdot}23$ Å) – this despite Cs being the heaviest atom in the formula unit. The large thermal motion is the result of the Cs atoms occupying big holes. The nearest-neighbour distances of Cs (Cs–N; 3·55 and 3·86 Å) are much larger than their combined interatomic radii (3·24 Å) (Slater, 1964); this also explains the high thermal motion of N atoms perpendicular to the Li–N bonds. In this connexion it is worth mentioning that the instability of the cubic structure has been attributed to the large Cs hole and high Cs thermal motion (Ryan & Swanson, 1974). Transition to the tetragonal phase allows rearrangement of the $Cr(CN)_6$ group in such a way as to reduce the Cs hole size. The situation can be compared with the ABO_3-type perovskites [the cubic structure of $Cs_2LiM(CN)_6$ can be considered to be a double perovskite], where the small B ion occupies a relatively large hole, thereby rendering the structure unstable and causing successive structural phase transitions with temperature. $KNbO_3$ provides a good example of such a case (Hewat, 1973). In the tetragonal phase, although the interatomic distances Cs–C(1) and Cs–C(2) are somewhat reduced compared to the cubic phase value (Table 2), the Cs hole size is still much larger than the sum of the nearest-neighbour interatomic radii. This, together with the high thermal motion exhibited by the Cs atoms, points to the potential instability of the tetragonal structure. We have collected neutron diffraction data at low temperatures. The powder profile at 4·2 K bears definite evidence of non-tetragonality of the structure, thus confirming further structural phase transformation. Detailed analysis of these data is yet to be completed.

Part of the work was completed during the period when one of us (MRC) was on an attachment from the J. J. Thompson Physical Laboratory, University of Reading. The authors are indebted to Dr M. J. Cooper for helpful comments, especially in the selection of the space group. Thanks are also due to Professor E. W. J. Mitchell for his continued interest in the work. Help and assistance provided by the PLUTO reactor staff in the neutron data collection are gratefully acknowledged.

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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 $P2_1/n$, $Z = 4$, $a = 16{\cdot}022\,(6)$, $b = 20{\cdot}418\,(10)$, $c = 15{\cdot}671\,(8)$ Å, $\beta = 89{\cdot}46°\,(4)$] 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 $P2/n$, $Z = 2$, $a = 16{\cdot}073\,(2)$, $b = 10{\cdot}126\,(1)$, $c = 14{\cdot}417\,(2)$ Å, $\beta = 96{\cdot}09°\,(1)$] was solved by the Patterson method. The R index was 4·6% including H atoms. In these complexes, the average distances $Cs^+ \cdots O$(carbonyl) are longer than $Cs^+ \cdots O$(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^+ ($\Delta G_H^o = -76{\cdot}5$ kcal mol^{-1}) compared with that of Na^+ ($-96{\cdot}5$ kcal mol^{-1}) (Prestegard & Chan, 1970). However, in spite of the larger difference in ΔG_H^o 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 complex (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 $Cs^+ \cdots O$ bond was observed at a lower frequency region than that of the $K^+ \cdots O$ 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-

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