Fig. 2. Comparison of the orientation of $Cr(CO)_3$ relative to the dihydropyridine ring in complexes (I) − (IV). The viewing direction is along the C_3 axis of the $Cr(CO)_3$ group. Note that the original paper on (III) (Bear & Trotter, 1973) employs a different numbering system and the opposite enantiomorph.

the formation of (II) over its hitherto unobserved structural isomer.

Unlike (I) and (II), each being a racemate, (IV) crystallizes in a noncentrosymmetric space group. The crystal lattice is built of molecules of the same chirality, with either the $(2S,2'R)$ configuration (as depicted in the structural formula and in Fig. 1) or the enantiomeric $(2R,2'S)$ configuration. This has been confirmed

by measuring the optical activity of individual single crystals.

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On the Absolute Configuration of the Tris(ethylenediamine)nickel(II) Cation. I. The Structure and Absolute Configuration of (−)-[Ni(en)₃](NO₃)₂*

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Abstract

The X-ray crystal structure of $[Ni(en)_3](NO_3)_2$ has been redetermined in order to correlate the absolute configuration with the sign of the optical rotatory strength in the region of the Ni^{II} d–d transitions (*i.e.* 10 000 to 30 000 cm^{-1}). The space group is hexagonal, $P6_3 22$, with $a = 8.872$ (3), $c = 11.359$ (3) Å, and $Z = 2$. The structure was refined by full-matrix least squares to a final R value of 0.022. The absolute configuration, determined by the Bijvoet method based on the anomalous dispersion of Ni, shows the $[Ni(en)_3]^{2+}$

* The symbol (−) preceding the chemical formula refers to the sign of *all* of the d–d transitions when measured with light normal to the ab plane of polished single-crystal plates.

[$\Delta(\lambda\lambda\lambda)$; lel_3] cation to be associated with (−) signs for the rotatory strengths of all the d–d transitions. Independent experiments on a number of samples confirm this conclusion. The bond lengths and angles observed are similar to those of related [M(en)$_3$] cations. The N—C—C—N torsional angle is −53·2°. There is an extensive hydrogen-bonding system between the −NH$_2$ H atoms and the nitrate O atoms. Eight nitrates surround each [Ni(en)$_3$] cation, with each amino H atom shared, in a bifurcated manner, by two nitrate O atoms. The molecular packing is such that the nitrates are staggered along the threefold crystallographic axes, allowing closest packing.

Introduction

The absolute configurations of large numbers of classical Werner coordination compounds, particularly of Co^{III}, are known. The first one studied was the [Co(en)$_3$]$^{3+}$ cation, whose structure and absolute configration were determined by Saito, Nakatsu, Shiro & Kuroya (1955) in the form of the double salt (+)$_{589}$-2[Co(en)$_3$Cl$_3$].NaCl [$\Delta(\delta\delta\delta)$]. This study constituted the first determination of the absolute configuration of a transition-metal complex by the Bijvoet method (Bijvoet, Peerdeman & van Bommel, 1951). Since then, the number of such structure and absolute configurational determinations has increased rapidly. The field has been reviewed recently by Saito (1978).

The tris(ethylenediamine)nickel(II) cation has been known since 1899 (Werner & Megerle, 1899; Werner, 1899), yet its absolute configuration has never been determined since it is kinetically labile and the classical methods of resolution are unsuitable for either single-crystal growth or for the measurement of chiro-optical properties in fluid media. However, owing to the unusual circumstance of spontaneous resolution of the complex upon crystallization as the dinitrate salt, and the fact that the space group is uniaxial as well as enantiomorphic, the circular dichroism of the single crystals may be determined. This offers the opportunity for direct correlation of the sign of the rotational strength with the absolute configuration as determined by the Bijvoet method. The results of such correlations are given below.

Experimental

[Ni(en)$_3$](NO$_3$)$_2$, (I), is readily prepared by slow evaporation of aqueous solutions of Ni(NO$_3$)$_2$ containing an excess of ethylenediamine. Crystals were grown at room temperature (ca 295 K) from saturated aqueous solutions of racemic mixtures, since the substance is self-resolved by this procedure. Data were collected from a crystal cleaved from a nearly

Table 1. *Crystallographically important data-collection and data-processing information*

Empirical formula	C$_6$H$_{24}$N$_8$NiO$_6$
Molecular weight	363·022
Cell constants	$a = 8.872$ (3) Å
	$c = 11.359$ (3)
Unit-cell volume	$V = 773.98$ Å^3
Space group	$P6_3 22$
Density (measured)	$d_m = 1.560$ (3) Mg m^{-3}
(calculated)	$d_c = 1.557$
Absorption coefficient (Mo $K\alpha$)	$\mu = 1.224$ mm^{-1}
Radiation used for data collection	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
Scanning range for 2θ	$4 \le 2\theta \le 70°$
Crystal mounted along	Approximately [001]
Standards for intensity control (every 2 h of exposure time)	602 and 433
Scan width for each reflection	$\Delta\theta = (1.10 + 0.35 \tan \theta)°$
Maximum scan time	300 s
Prescan acceptance criterion for classifying observed reflections	$[\sigma(I)/I]$ prescan ≤ 1.90
Scan technique	ω–2θ, bisecting
Total number of reflections collected*	741
Number of contributing reflections in the last least-squares cycle	452
Number of variables	48
Weighting scheme	$w = [\sigma(F_o)]^{-2}$
Final $R(F)$†	0·022
Final $R_w(F)$‡	0·028

* There were 741 unique data of which 452 were found to have $I > 3\sigma(I)$. This latter set was used for all subsequent calculations.
† $R(F) = \sum (||F_o| - |F_c||)/\sum |F_o|$.
‡ $R_w(F) = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

hexagonal (cross section) column which was several mm long. The dark-purple substance crystallizes in the hexagonal space group $P6_3 22$ (Swink & Atoji, 1960) and its chiro-optical characteristics have been established by Palmer & Yang (1975, 1978). We have now begun a collaborative study of the relationship between absolute configurations and optical activities of [M^{II}(en)$_3$](NO$_3$)$_2$ salts (M^{II} = Mn, Co, Ni, Cu, Zn, etc.). Elsewhere, we (Palmer & Bernal, 1980) will present a correlation between CD spectra in the solid state and the absolute configurations of these substances as determined by the Bijvoet method. These results will be compared to those deduced by optical correlation (Palmer & Yang, 1975).

The crystal was mounted on a translation (x,y,z) goniometer head attached to a computer-controlled CAD-4 diffractometer. Data were collected using techniques described elsewhere (Reisner, Bernal & Dobson, 1978). Table 1 lists the details of data collection which are unique to this study, as well as details and parameters of data processing and refinement. The data were not corrected for absorption since the absorption coefficient is small (see Table 1). The crystal used was a distorted hexagonal column elongated along c and truncated by (00$\bar{1}$) and (1$\bar{1}$1); the columnar faces were the six forms of {100}, {010} and

{1$\bar{1}$0}. The smaller faces, indicative of faster growth in these directions were (010), ($\bar{1}$00) and (1$\bar{1}$0). The shortest and longest cross-sectional dimensions were 0·20 and 0·50 mm while the length of the column was 0·70mm.

Solution of the structure and refinement

Swink & Atoji (1960) reported the crystal structure of (I) but did not determine its absolute configuration despite the fact that it crystallizes in the space group $P6_322$, an unambiguous, noncentrosymmetric space group. This was caused by their inconclusive measurements of the optical rotation of this substance in solution and in the crystalline state (see Palmer & Yang, 1975, 1978). Failing to observe any rotation of the plane of polarized light, Swink & Atoji (1960) were led to state that 'the results of these observations indicate that the crystal is racemic'.

Crystallographically, it should be impossible for crystals to consist of racemic pairs of cations since the asymmetric unit is $\frac{1}{6}$ of the [Ni(en)$_3$]$^{2+}$ cation, that is, unless there is disorder of a statistical type in the lattice such that each site has 50% occupancy by two enantiomers; *i.e.* each lattice site is occupied half the time by $\Delta(\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta)$ configurated pairs (or another suitable pair) of antipodes. No such disorder was reported by Swink & Atoji (1960). Furthermore,

disorder of that sort would produce 'averaged' conformations of the inherently non-planar Ni(en) five-membered rings. The structure reported by Swink & Atoji gives a completely ordered, non-planar Ni(en) five-membered ring 'with the azimuthal angle of 45·8 $\pm$ 2·0° between the planes determined by the C—C and C—N bonds'. Using single crystals, we have tested the possibility of disorder in a number of crystals of [Ni(en)$_3$](NO$_3$)$_2$ and [Zn(en)$_3$](NO$_3$)$_2$ (the latter compound is isomorphous and isostructural with the Ni species; Korp & Bernal, 1980) grown here and at Duke University and have found no examples of disordered crystals. The space group and cell constants given by Swink & Atoji are correct, as are the coordinates of the atoms they reported, including the approximated positions of the H atoms. We used their coordinates as a starting set and the least-squares fitting converged in a few cycles of isotropic refinement. Conversion to anisotropic thermal parameters for the non-hydrogen atoms while retaining isotropic motion for the H atoms produced the final values listed in Tables 1 and 2.* The anomalous-dispersion coefficients of Cromer & Liberman (1970) were used for Ni.

As expected from the foregoing, the distances and angles derived from our refinement agree well with those reported earlier by Swink & Atoji (1960) and, therefore, their discussion of the structural parameters is still valid. The final bond distances and angles for the present study are given in Table 3.

Determination of the absolute configuration

When the structure had been refined completely, structure factors [$F(hkl)$ and $F(h\bar{k}\bar{l})$] were computed in order to locate a suitable Bijvoet set (Bijvoet, Peerdeman & van Bommel, 1951) to test the absolute configuration. Fifteen reflections were chosen which were measured, four times each in the order hkl, $\bar{h}\bar{k}\bar{l}$,

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34936 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^4$; *for* H $\times 10^3$)

Standard deviations are given in parentheses.

	x	y	z
Ni	6667	3333	2500
N(1)	4572 (2)	1399 (2)	3515 (2)
C	2958 (2)	1363 (4)	3150 (2)
N(2)	3333	6667	1108 (2)
O	2086 (3)	5173 (2)	1084 (2)
H(1)	199 (5)	33 (4)	342 (2)
H(2)	303 (5)	242 (4)	369 (2)
H(3)	449 (3)	43 (4)	346 (2)
H(4)	463 (5)	151 (4)	422 (3)

Table 3. *Intramolecular bond distances* (Å), *angles* (°) *and torsion angle* (°), *and hydrogen-bond distances* (Å) *and angles* (°)

Ni—N(1)	2·130 (2)	C—H(1)	0·94 (3)	N(1)—Ni—N(1″)	81·9 (1)	N(1)—C—C″—N(1″)	−53·2
N(1)—C	1·476 (3)	C—H(2)	1·09 (3)	Ni—N(1)—C	108·1 (1)		
C—C″	1·490 (5)	N(1)—H(3)	0·83 (3)	N(1)—C—C″	110·0 (2)		
N(2)—O	1·231 (2)	N(1)—H(4)	0·80 (3)				

H(3)···O′	2·45 (4)	H(3)···O″	2·81 (3)	H(4)···O‴	2·45 (3)	H(4)···O″‴	2·80 (4)
N(1)···O′	3·243 (4)	N(1)···O″	3·483 (3)	N(1)···O‴	3·200 (3)	N(1)···O″‴	3·454 (3)
N(1)—H(3) ···O′	160 (2)	N(1)—H(3) ···O″	140 (2)	N(1)—H(4) ···O‴	156 (4)	N(1)—H(4) ···O″‴	141 (4)

Symmetry code: (′) = 1 − y, −x, $\frac{1}{2}$ − z; (″) = x, x − y, $\frac{1}{2}$ − z; (‴) = y, y − x, $\frac{1}{2}$ + z; (″‴) = 1 + x − y, x, $\frac{1}{2}$ + z.

Table 4. *Comparison of* $[I(hkl)](+++)$ *vs* $[I(\bar{h}\bar{k}\bar{l})](---)$ *for two crystals of* $[Ni(en)_3](NO_3)_2$

Indices	Our crystal*	Palmer's crystal†	Predicted‡
	$I(+++)/I(---)$	$I(+++)/I(---)$	$F^2(+++)/F^2(---)$
$\bar{1}32$	$54\,K < 58\,K$	$69\,K > 63\,K$	$3{\cdot}0\,K < 3{\cdot}2\,K$
$1\bar{3}\bar{2}$	$61 > 58$	$64 < 69$	$3{\cdot}2 > 3{\cdot}0$
$2\bar{3}\bar{2}$	$50 < 52$	$65 < 66$	$3{\cdot}0 < 3{\cdot}2$
122	$64 > 60$	$58 < 66$	$3{\cdot}2 > 3{\cdot}0$
$12\bar{2}$	$63 < 66$	$55 < 64$	$3{\cdot}0 < 3{\cdot}2$
212	$61 < 65$	$57 > 52$	$3{\cdot}0 < 3{\cdot}2$
$21\bar{2}$	$65 > 61$	$59 < 63$	$3{\cdot}2 > 3{\cdot}0$
$\bar{3}52$	$16{\cdot}3 > 14{\cdot}4$	$44 < 50$	$0{\cdot}64 > 0{\cdot}55$
$\bar{3}5\bar{2}$	$14{\cdot}5 < 17{\cdot}0$	$50 > 42$	$0{\cdot}55 < 0{\cdot}64$
232	$18{\cdot}3 > 15{\cdot}5$	$42 < 50$	$0{\cdot}64 > 0{\cdot}55$
$23\bar{2}$	$15{\cdot}9 < 18{\cdot}7$	$50 > 43$	$0{\cdot}55 < 0{\cdot}64$
322	$15{\cdot}8 < 18{\cdot}1$	$46 > 40$	$0{\cdot}55 < 0{\cdot}64$
$32\bar{2}$	$18{\cdot}2 > 16{\cdot}0$	$43 < 48$	$0{\cdot}64 > 0{\cdot}55$
532	$13{\cdot}6 < 15{\cdot}9$	$45 > 40$	$0{\cdot}55 < 0{\cdot}64$
$53\bar{2}$	$16{\cdot}5 > 13{\cdot}9$	$40 < 46$	$0{\cdot}64 > 0{\cdot}55$

* This was the data crystal used in the current study.

† Palmer's crystal (see text) was used in his optical studies and is characterized by having $(+)$ signs for the rotations of the bands in the visible region which are associated with the d–d transitions of the Ni^{II}.

‡ Predicted ratios obtained from the model described by the coordinates listed in Table 2; *i.e.* the absolute configuration of the $[Ni(en)_3]$ cations is $\Delta(\lambda\lambda\lambda)$. See Figs. 1 and 2.
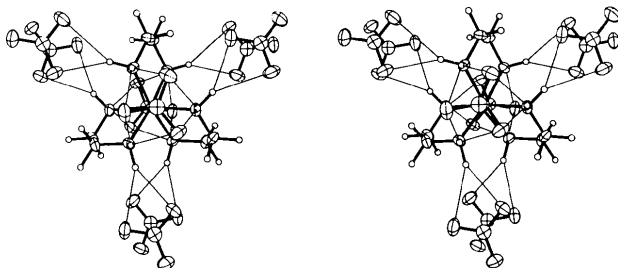

Fig. 1. View down the threefold axes showing all the hydrogen bonds (thin lines) to a single $[Ni(en)_3]^{2+}$ unit. The thermal ellipsoids are shown as 35% probability boundaries, with spheres of arbitrary diameter for the H atoms. Note the alternate orientations of the nitrates along each of the four threefold axes included in the view.
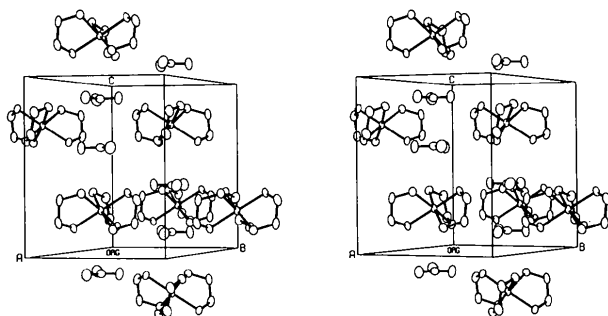

Fig. 2. Packing diagram of the contents of the unit cell (hydrogens omitted for clarity) showing the environment about the nitrate anions and the 6_3 arrangement of the cell components along the c axis.

hkl, $\bar{h}\bar{k}\bar{l}$, *etc.*, and suitably averaged. The results (Table 4) show that the choice of coordinates used in the refinement (Table 2) is correct. Such coordinates lead to the absolute configuration shown in Figs. 1 and 2, in which the $[Ni(en)_3]^{2+}$ cation has the $\Delta(\lambda\lambda\lambda)$ configuration.

A separate crystal of (I), which had been used by Palmer & Bernal (1980) for CD measurements, was sent to Houston as a blind sample (only an identifying label was provided). The same set of 15 reflections was measured and the ratios proved to be exactly the inverse of the original crystal (see Table 4). Professor Palmer informed Korp and Bernal that his crystal gave $(+)$ values for all the CD bands in the visible region (the d–d transition observable in the interval 10 000 to 33 000 cm^{-1}). Consequently, for $[Ni(en)_3](NO_3)_2$ single crystals, $(+)$ values of the absorption in the CD experiment are to be associated with a $\Delta(\delta\delta\delta)$ configuration for the cation. In the original crystal, the opposite must be true since it is the enantiomer of the crystal sent to Houston by Palmer. This result confirms the conclusion reached earlier by optical correlation (*via* the Ru^{II} analogue) with $[Co(en)_3]^{3+}$ (see Palmer & Yang, 1975, 1978).

Hydrogen bonding

Extensive and complex hydrogen bonding exists between the $-NH_2$ H atoms of the ethylenediamines and the O atoms of the nitrate anions. Although formally there are two nitrate anions per $[Ni(en)_3]^{2+}$ moiety, the packing in the lattice is such (see Figs. 1 and 2) that eight nitrates are arranged about the cations and each amino H atom is shared in an unusual, bifurcated manner by two O atoms. At the same time, each O has five close approaches by H atoms – two from amino H atoms lying almost exactly in the plane of the nitrate anions (2·27 and 2·81 Å), two from amino H atoms lying above or below the plane of the anion (2·45 and 2·80 Å), and one contact from a methylene H located 2·43 Å away. This last contact, probably not a true hydrogen bond, has a geometry (see Fig. 1) such that the N—O··· H angle is nearly 180° which would make no sense from a molecular-orbital argument. Nonetheless, it is a close-packing contact. Table 3 also contains a summary of the hydrogen-bonding parameters. Although the N···O distances seem rather long for normal hydrogen bonds, they are not unusual for bifurcated contacts, as is the case in this compound.

The molecular-packing diagram shown in Fig. 2 displays the environment about the nitrate anions and shows that the pairs of adjacent anions stacked along the crystallographic threefold axes are twisted almost 60° from each other so as to stagger the O atoms and allow the closest possible packing. The $N(2)\cdots N(2)$ spacing is 3·16 Å. Also, the skeletal canting of the

ethylenediamines is such that the two amino surfaces, located on opposite ends of the cationic group and with the threefold axis normal to them, are staggered by approximately the same amount, giving additional stability to the observed packing scheme.

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Crystal Structure of Hydrated Barium Cytidine 5'-Phosphate, Ba₂(C₉H₁₂N₃O₈P)₂(8·5H₂O)₂. Crystal Packing and Conformational Homologies in Alkali-Metal– and Alkaline-Earth-Metal–Ribonucleotide Complexes

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Abstract

Hydrated barium cytidine 5'-phosphate [Ba(5'-CMP).8·5H₂O] crystallizes in the orthorhombic space group $P2_12_12$ with two independent molecules in the asymmetric unit. The unit-cell dimensions are $a = 20·984$ (5), $b = 23·168$ (8) and $c = 8·940$ (10) Å; $Z = 8$. The structure was solved by the heavy-atom method and refined to an R value of 0·128 using anisotropic temperature factors for Ba and P and isotropic temperature factors for the other atoms. The two independent nucleotides exhibit very similar overall conformations, *viz* C(2')-*endo*, C(1')-*exo* ($^2T_1$), (χ) *anti*, and (ψ) *gauche*⁺. One of the Ba²⁺ ions is in a general position coordinated to the carbonyl O of a cytosine and seven water oxygens. The other is distributed on two different diad axes and coordinated to the *cis* hydroxyls of the riboses and water molecules.

The two independent molecules are related by a pseudo twofold axis passing roughly through ($\frac{1}{4}$,0,$\frac{1}{4}$) midway between the 2_1 axes running parallel to the b axis. The crystal structure is highly hydrated with 18 independent water *sites* in the asymmetric unit, two of which are on diad axes. The crystal packing is dominated by alternating chains of nucleotides and barium–water columns. It is observed that the known alkali-metal– and alkaline-earth-metal–ribonucleotide complexes, crystallizing in either primitive or centered orthorhombic lattices, exhibit a striking similarity in packing scheme, regardless of whether they bear a pyrimidine or a purine base.

Introduction

Cytidine 5'-monophosphate (5'-CMP) is one of the four common ribonucleotides which make up ribonucleic acids (RNA's). The crystal structure of the barium salt of cytidine 5'-monophosphate 8·5 hydrate

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