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The Crystal Structure of Triethylenediaminenickel(II) Nitrate, $Ni(NH_2CH_2CH_2NH_2)_3(NO_3)_2$*

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The crystal structure of triethylenediaminenickel(II) nitrate, $Ni(NH_2CH_2CH_2NH_2)_3(NO_3)_2$, is hexagonal D_6^6–$P6_322$ with two chemical formulae in a unit cell of dimensions $a = b = 8{\cdot}87$ and $c = 11{\cdot}41$ Å, confirming results previously reported. The packing of the $[Ni(en)_3]^{++}$ and NO_3^- groups in the crystal is of extreme interest. Two nitrate ions are stacked one above the other to form a close packing with the complex ions. Although this configuration would seemingly give rise to electrostatic instability, a stable crystalline field is achieved, apparently by interactions involving the hydrogen atoms, some of which participate in forming a weak bifurcated hydrogen bond of the type, $O \cdots (H\text{–}N)_2$. The configuration of $[Ni(en)_3]^{++}$ is D-*lll* or L-*ddd* type with Ni–N = 2·12 Å, N–C = 1·50 Å and C–C = 1·50 Å. The configuration of the Ni(en) ring is a gauche–gauche–gauche type with the azimuthal angles of 46° and 56°. Considerable distortion of the octahedral coordination in $[Ni(en)_3]^{++}$ is observed. The N–O distance in NO_3^- is 1·21 Å. The optical properties and the infra-red spectrum of the compound are also discussed.

Introduction

In metal chelate compounds, if chelation can take place to form five-membered rings, the stability of the complex ions is greatly enhanced. Ethylenediamine, abbreviated (en), is the simplest and most important of such bases, and its compounds have played an important part in the development of coordination theory. Accordingly, the ethylenediamine complex compounds have been the subject of various investigations.

The crystal structures of $[Cu(en)_2][Hg(SCN)_4]$ (Scouloudi, 1953), $[Co(en)_2Cl_2]Cl.HCl$ (Nakahara *et al.*, 1952), $[Co(en)_3]Cl_3.3\,H_2O$ (Nakatsu *et al.*, 1956) and 2 D-$[Co(en)_3]Cl_3.NaCl.6\,H_2O$ (Nakatsu *et al.*, 1957) have been reported and the absolute configuration of $[Co(en)_3]^{+3}$ has been determined using the X-ray dispersion method (Saito *et al.*, 1957). However, no complete structure determination of a complex salt containing the $[Ni(en)_3]^{++}$ ion has yet been reported.

A preliminary study on the crystal structure of $[Ni(en)_3](NO_3)_2$ has shown that the crystal is hexagonal D_6^6–$P6_322$ with two chemical formulae in a unit cell of dimensions $a = b = 8{\cdot}87 \pm 0{\cdot}01$, $c = 11{\cdot}41 \pm 0{\cdot}02$ Å (Watanabe & Atoji, 1951). They also reported that the crystal is spiral with a pitch of 3°/cm. along the *c* axis. Only one other spiral crystal, urea oxalate, is known (Lonsdale, 1945). The present study was undertaken in order to re-examine the previous results and to complete the three-dimensional structure analysis of the compound.

Experimental

An aqueous solution of $[Ni(en)_3](NO_3)_2$ was prepared by dissolving nickel nitrate in water and slowly adding a stoichiometric quantity of commercially-available 98% ethylenediamine. Single crystals with the external morphology of an elongated hexagonal pyramid were obtained by allowing this solution to evaporate slowly at room temperature. Cooling the crystal from room temperature to liquid nitrogen temperature is accompanied by a change from deep violet to pale violet. If heated slowly, the crystal decomposes at 270 °C., but with rapid heating the decomposition becomes explosive in nature.

When viewed with a polarizing microscope, the crystals exhibited no apparent optical rotation. Moreover, the phenomena characteristic of optically active crystals were not observed in the conoscope interference figure (Tutton, 1922). The results of these observations indicate that the crystal is racemic. This was confirmed by the fact that a solution of the crystal exhibited no optical rotation. However, Airy's spiral (Tutton, 1922) was not observed in the interference figure of the crystal. This implies that the linear dimensions of the optically active domains are probably not larger than about 10^{-4} cm. In order to check the vibrational spectra of the N–H bond in (en) for the possibility of hydrogen bonding, infra-red spectra were obtained for powder samples using both the KBr-pellet and Nujol–Mull techniques. The wavelengths indicated on the recorder were calibrated against the infra-red spectrum of polystyrene.

Single crystals were formed into nearly perfect cylinders of approximately 0·3 mm. in diameter and

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with axes along [001] and [110]. The diameter of the cylinder was chosen so that the maximum absorption correction to the intensity should be less than 5% for Mo *Kα* radiation.

The Laue photographs indicated that our crystals are also spiral with pitch in approximate agreement with the value previously reported. Precession intensity data were obtained for the $\{h0l\}$, $\{hhl\}$ and $\{h,2h,l\}$ zones using the successive timed exposure method with Mo *Kα* radiation. The equi-inclination Weissenberg data for the $\{hhl\}$ zones with $l=0$ to 9 and the $\{hhl\}$ zones with $h=0$ to 5 were recorded on multiple films with the successive timed exposure technique and Mo *Kα* radiation. The intensities were estimated visually by two independent observers with the aid of the standard intensity scales. The set of judgments with the best internal consistency was chosen for the structure refinement. Lorentz and polarization corrections were applied to the intensity data using the IBM 650 computer.

Structure determination

The lattice constants and the space group obtained in the present study were in agreement with those previously reported. The reflections for which $h-k=3n$ and $l=2n$ were found to be relatively stronger than the others, and those for which $h-k=3n$ and $l\neq 2n$ were generally much weaker than the other reflections. This led to the postulation that the nickel atoms occupy either of the two-fold positions, 2(*c*) or 2(*d*), at each of which the point symmetry is D_3-32 (*International Tables*, 1952). This assumption was readily verified by the strong vector-interactions in the [001] and [010] projections of the Patterson function.

If the internal symmetry of the chelating molecule is disregarded, there are two optical isomers of the $[Ni(en)_3]^{++}$ ion, D-$[Ni(en)_3]^{++}$ and L-$[Ni(en)_3]^{++}$. Here, the conventions used in naming the optical isomers are based on the absolute configurations of $[Co(en)_3]^{+3}$ (Saito *et al.*, 1957). As found in other (en) complex compounds, it can readily be shown that a planar configuration of the ligand molecule is not probable in $[Ni(en)_3]^{++}$, unless a prohibitive distortion of the (en) molecule is allowed. Subsequently, there are two possible optical isomers of the ligand, *d*-(en) and *l*-(en). Thus, a total of eight optical isomers, D-*ddd*, D-*ddl*, D-*dll*, D-*lll*, L-*lll*, L-*lld*, L-*ldd* and L-*ddd*, are conceivable (cf. Nakatsu *et al.*, 1956). However, only four configurations, D-*ddd*, D-*lll*, L-*lll* and L-*ddd*, are possible in the crystal because of the required point symmetry, D_3-32. It should be noted that of these four isomers, there are two sets, (D-*ddd*, L-*lll*) and (D-*lll*, L-*ddd*), which are distinguishable in the projections along the [001] and [100] axes. The nitrogen atoms in the nitrate ion, denoted by N′, may be assigned either to any two of the three two-fold sets, 2(*c*), 2(*b*) and 2(*a*), or to one of the four-fold sets, 4(*f*) and 4(*e*).

Using the $\{hk0\}$ and $\{0kl\}$ data and the IBM 650 computer, the least-squares convergence test was used for selecting the possible structure. All models with the N′ atoms in the 4(*e*) positions or in two of the three two-fold positions failed to give an *R*-factor of less than 30%. Only the structure with N′ at 4(*f*) and $[Ni(en)_3]^{++}$ of a (D-*lll*, L-*ddd*) form gave satisfactory convergence leading to an *R* factor of less than 10% for approximately 200 $\{hk0\}$ and $\{0kl\}$ reflections. The three-dimensional structure is subject to the following ambiguities:

(*a*) The optically active domains, each consisting of only one of the possible optical isomers, D-*lll* or L-*ddd*, are larger than the coherent X-ray scattering domains. In this case, since D-*lll* and L-*ddd* are enantiomorphous to one another, the $\{hkl\}$ structure factors could be treated as if there were only one isomer in the crystal.

(*b*) The distribution of the D-*lll* and L-*ddd* structures has long-range order within the coherent X-ray scattering domains. If so, the Laue function will give sharp, but possibly very weak, intensity maxima at interstitial points of the original reciprocal lattice.

(*c*) There is short-range order in the distribution of the isomeric forms within the coherent domains. In this case, non-Laue–Bragg scattering maxima would be expected in the interstices of the reciprocal lattice.

(*d*) A statistical structure is also conceivable. This model implies a completely disordered distribution of the isomeric forms within the coherent domains.

A careful examination of the diffraction patterns revealed no interstitial-type reflections. Moreover, no intense diffuse scattering was observed except some due probably to the lattice vibrations (Watanabe & Atoji, 1951). The possibilities described in (*b*) and (*c*) could, therefore, be eliminated. If the statistical structure (*d*) were correct, the $\{hkl\}$ data would not give a unique set of atomic parameters. However, non-statistical atomic parameters obtained from the $\{hk0\}$ and $\{h0l\}$ refinement gave satisfactory convergence in the $\{hkl\}$ least-squares treatment. The final *R*-factor for 350 Weissenberg $\{hkl\}$ reflections was 7·8%. The final atomic coordinates, their standard deviations, and the individual isotropic temperature factors are listed in Table 1. The observed and calculated structure factors based on the parameters given in Table 1 are listed in Table 2.* The hydrogen coordinates listed in

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* Table 2, comprising 7 pages of typescript, has been withdrawn and is deposited as Document No. 6046 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document Number and by remitting \$1·25 for photoprints, or \$1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 1 were obtained from assumptions that the carbon and nitrogen form tetrahedral bonding with the hydrogen atoms and that the C–H and N–H bond distance are 1·09 Å and 1·01 Å as found in the methane and ammonia molecules, respectively (Sutton, 1958). It is not likely that the hydrogen coordinates in Table 1 are greatly different from the true values, since no ambiguity is involved in determining the hydrogen configuration. The least-squares refinements including hydrogen atoms indicated no appreciable improvement in the R-factor.

Table 1. *Atomic co-ordinates, their standard deviations and temperature-factor coefficients in* $\exp\{-B(\sin\theta/\lambda)^2\}$

Atom	B (Å^{-2})	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ni	1·26	2/3	1/3	1/4	—	—	—
N	3·02	0·4588	0·1402	0·3507	0·0017	0·0015	0·0016
C	3·62	0·2911	0·1290	0·3140	0·0018	0·0023	0·0017
N′	1·37	1/3	2/3	0·1110	—	—	0·0015
O	5·16	0·2117	0·5189	0·1110	0·0016	0·0016	0·0018
H_{I}		0·186	−0·003	0·333			
H_{II}		0·274	0·223	0·364			
H_{III}		0·451	0·024	0·339			
H_{IV}		0·479	0·173	0·437			

The atomic scattering factors of carbon, nitrogen and oxygen used for the present study were those based on the Hartree–Fock or Hartree method (Berghuis *et al.*, 1955). However, no scattering factor based on the self-consistent field is available for Ni^{++}. Therefore, the average of the Pauling–Sherman (1932) and Thomas–Fermi–Dirac values (1957), which has been proved to be a close approximation to the Hartree value, was used as the scattering factor of Ni^{++}.

Discussion of the structure

The packing of the $[Ni(en)_3]^{++}$ and $(NO_3)^-$ groups in the crystal is of extreme interest. As is shown in Figs. 1 and 2, where the hydrogens are omitted for the sake of clarity, two nitrate ions are stacked one above the other to form a close packing with the complex ions. The close proximity of the two negatively charged groups would seemingly give rise to some degree of electrostatic instability. The stability of the crystal nevertheless implies that a stable crystalline field is achieved in the structure. Obviously, any consideration of the complete interatomic potential field must include all interactions involving the hydrogen atoms. Consequently, the interatomic distances, including those involving the hydrogen atoms, were calculated using the atomic coordinates listed in Table 1.

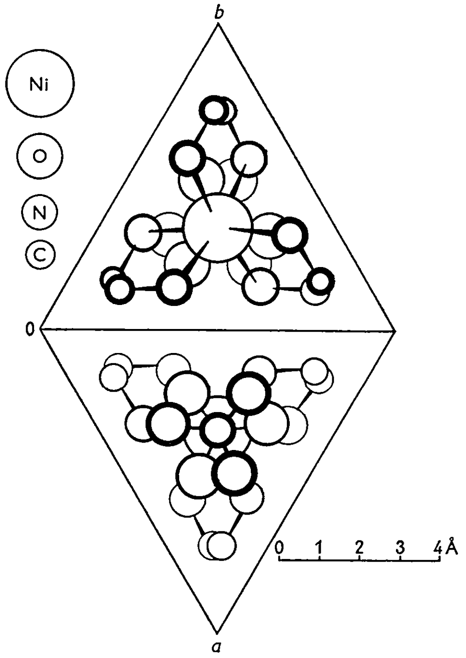

Fig. 1. The [001] projection of L-*ddd*-$[Ni(en)_3](NO_3)_2$.

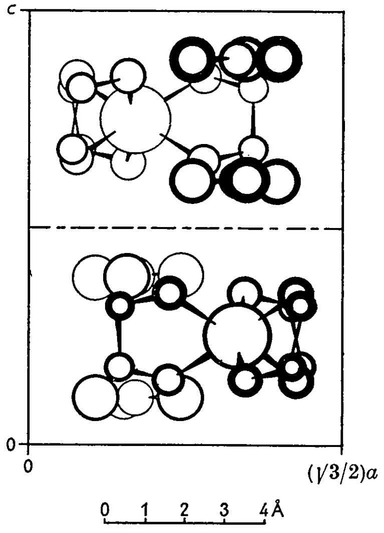

Fig. 2. The [010] projection of L-*ddd*-$[Ni(en)_3](NO_3)_2$.

The interatomic distances and angles within the $[Ni(en)_3]^{++}$ ion are listed with their standard deviations in Table 3. The difference between the observed Ni–N bond distance of 2·12 Å in $[Ni(en)_3]^{++}$ and the reference value of 2·09 Å (Pauling, 1948) is probably not significant. The N_{I}–Ni–N_{II} and N_{II}–Ni–N_{III} bond angles deviate significantly from 90°, and the difference between the distance $N_{I}\cdots N_{II}$ and $N_{I}\cdots N_{III}$ or $N_{II}\cdots N_{III}$ is also significant. In summary, the octahedral coordination bonds formed by the nickel atoms with the nitrogens in the (en) groups are considerably distorted from the normal d^2sp^3 configuration. In the $[Co(en)_3]^{+3}$ ions (Nakahara *et al.*, 1952; Nakatsu *et al.*, 1956; Nakatsu *et al.*, 1957), this distortion appears to be smaller than that found in $[Ni(en)_3]^{++}$. In all known structures with $M(en)_3$, where M denotes the central atom, the angles

N_I–M–N_{III} and N_{II}–M–N_{III} are always larger than the angle N_I–M–N_{II}. The C–N and C–C distances in the (en) group are probably not significantly different from the single-bond distances. The chelating molecule assumes a gauche configuration with the azimuthal angle of 45·8 ± 2·0° between the planes determined by the C–C and C–N bonds. Values of 45° and 48° have been reported for this angle in $[Co(en)_3]Cl_3.3\,H_2O$ (Nakatsu *et al.*, 1956) and $2D\text{-}[Co(en)_3]Cl_3.NaCl.6\,H_2O$ (Nakahara *et al.*, 1952), respectively. The azimuthal angle between the plane determined by the C–C and C–N bonds and that determined by Ni–N and C–N bonds is 56°. Consequently, the configuration of the five-membered Ni(en) ring can be assigned as gauche–gauche–gauche, with respect to the N–C, C–C and C–N bonds.

Table 3. *Interatomic distances and angles within* $[Ni(en)_3]^{++}$

Ni–N	2·120 ± 0·013 Å	∠ Ni–N–C	109·7 ± 1·2°
C–N	1·500 ± 0·025	∠ N–C–C	111·1 ± 2·3
C–C	1·498 ± 0·028	∠ N_I–Ni–N_{II}	82·3 ± 1·0
$N_I \cdots N_{II}$	2·790 ± 0·025	∠ N_I–Ni–N_{III}	91·2 ± 1·0
$N_I \cdots N_{III}$	3·030 ± 0·025	∠ N_{II}–Ni–N_{III}	93·4 ± 1·0
$N_{II} \cdots N_{III}$	3·086 ± 0·025		

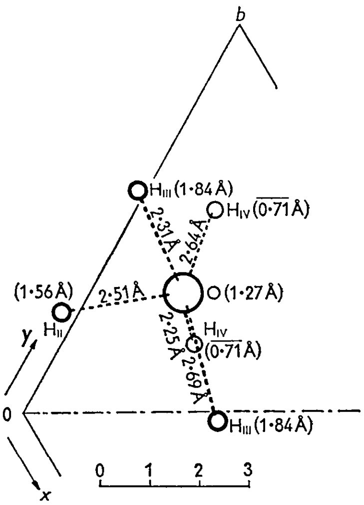

Fig. 3. The five hydrogens surrounding oxygen. The z-parameters of atoms in Å are shown in parentheses.

The NO_3^- group is planar within experimental error and the N′–O distance is 1·21 ± 0·01 Å in agreement with the standard empirical value (Pauling, 1948). Each oxygen atom is surrounded by five hydrogen atoms within a radius of 2·7 Å, as shown in Fig. 3. Three of the distances, 2·51, 2·65 and 2·69 Å, shown in Fig. 3, may be regarded as van der Waals contact (Pauling, 1948). However, two of the distances shown, 2·31 and 2·25 Å, are definitely shorter than those to be expected from the dispersion type of force only. Both of the hydrogens associated with the short $H \cdots O$ distances belong to nitrogen atoms. A schematic illustration of the environment of the NO_3^- group is given in Fig. 4. Each of the hydrogens in NH_2 has one oxygen neighbor at about 2·3 Å. If the formal electric charge of the NO_3^- group be denoted by $-\varepsilon$, from consideration of the resonance structures of NO_3^- the effective charge on each oxygen might be taken as $-\frac{1}{3}\varepsilon$ (Pauling, 1948). If the formal charge of the $[Ni(en)_3]^{++}$ group be equally distributed to the hydrogens in NH_2, then each of these hydrogen atoms would have an effective charge of $+\frac{1}{6}\varepsilon$. Since each oxygen atom has two hydrogen neighbors at about 2·3 Å, these postulated charges would tend to neutralize one another through localization of the formal charges. In this fashion, the effective charge on the NO_3^- groups could be made small enough to allow the unusual $NO_3^- \cdots NO_3^-$ packing described earlier. The closest approach of oxygens in two different NO_3^- groups was found to be 3·3 Å, as compared to the $O \cdots O$ van der Waals distance of 2·8 Å. Moreover, the two proximate NO_3^- groups are staggered to one another in their relative configuration. These indicate the presence of some residual effective charge on the NO_3^- groups.

The packing around the axis parallel to the c-axis and passing through the origin consists of hydrogens only. The closest $H \cdots H$ distance in this packing is 2·35 Å, as compared with the van der Waals $H \cdots H$ distance of 2·4 Å, indicating pure dispersion-type forces. Since these hydrogens are all those associated with the carbon atoms in (en), it seems that this part of the ligand contains little or none of the effective charge of the complex ion. This adds support to the charge postulation described earlier.

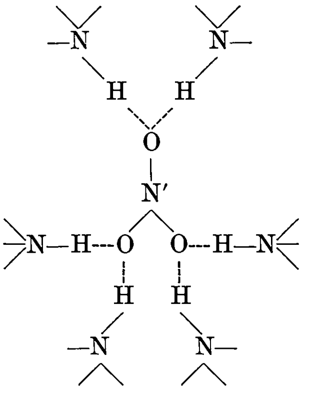

Fig. 4. Schematic representation of the neighborhood of the NO_3 group.

The configuration illustrated in Fig. 4 may be considered as a weak bifurcated hydrogen bond of the type $O \cdots (H\text{–}H)_2$. The infra-red spectrum of the powdered crystals of $[Ni(en)_3](NO_3)_2$ shows a fairly sharp peak with double maxima at about 3200 cm.$^{-1}$ and 3300 cm.$^{-1}$, respectively, for the symmetric and asymmetric stretching frequencies of the N–H bond. The corresponding frequencies of the gaseous ammonia molecule are 3337 cm.$^{-1}$ and 3414 cm.$^{-1}$

(Herzberg, 1945). Therefore, the N–H bonds in the ligands are not largely affected by the bifurcated hydrogen bond. This is reasonable, since the interaction due to the bifurcated hydrogen bond is generally quite small in comparison with the usual hydrogen bond. However, more precise infra-red study using a single crystal would be of great value in revealing the detailed nature of the interaction.

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Ordre Logarithmique de Densités de Repartition. II. Quelques Applications

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Several examples of logarithmic ordering of joint distribution functions of structure factors are given. The introduction of the notion of 'statistical chains combined with logarithmic ordering allow the determination of the sign of a triple product and of an invariant reflexion.

The maximal properties of logarithmically ordered joint distribution functions serve to establish a new criterion for selecting the 'right' set of signs for combinatorial procedures.

Introduction et plan

Pour illustrer la théorie que nous venons de développer (Bertaut, 1959, 1960), nous allons étudier d'abord les problèmes classiques des densités de répartition de deux et de trois facteurs de structure (III). La théorie gagne de l'intérêt dans l'étude de l'ensemble de quatre triple produits, correspondant à six facteurs de structure (IV). Mais c'est surtout l'introduction de la notion de '*chaîne statistique*', c'est-à-dire d'un *ensemble de facteurs de structure*, lié par certaines conditions qui nous permet de rendre la théorie réellement statistique, et de l'appliquer à la détermination de signes d'un triple produit ou d'un facteur de structure invariant. (V).

Enfin nous étudions quelques propriétés maximales de la densité de répartition de plusieurs facteurs de structure. Nous déterminons le niveau de probabilité de la structure la plus probable et nous présentons un nouveau critère pour le choix de la 'bonne' solution quand on emploie des méthodes combinatoires pour la détermination des signes (VI).

Cas de 2 facteurs de structure

On posera:

$$E_1=E(2h);\quad E_2=E(h)\,. \tag{III–1}$$

La fonction caractéristique est donnée par (II–25) avec

$$T_3=\tfrac{1}{2}\varkappa_{12}v_1v_2^2;\quad T_4=(1/4!)(\varkappa_{40}v_1^4+\varkappa_{04}v_2^4);$$
$$T_5=1/(3!2!)\,\varkappa_{32}v_1^3v_2^2+(1/4!)\,\varkappa_{14}v_1v_2^4\,. \tag{III–2}$$

Les polynômes $K_p(q)$ (II–30) servant à déterminer Q_i (II–29) s'évaluent aisément (cf. Appendice C). On a

$$\begin{aligned}
&K_3(1)=(1/2!)\varkappa_{12}A_1(A_2^2-1);\\
&K_3(2)=-(\varkappa_{12}/2!)^2(2A_1^2(2A_2^2-1)+H_4(A_2));\\
&K_3(3)=\varkappa_{12}^3A_1(A_1^2(3A_2^2-1)+\tfrac{3}{2}f_4);\\
&K_{3,4}(1,1)=-(1/3!2!)\varkappa_{12}(\varkappa_{40}H_3(A_1)H_2(A_2)+\varkappa_{04}A_1f_4);\\
&K_5(1)=(1/3!2!)\varkappa_{32}H_3(A_1)H_2(A_2)+(1/4!)\varkappa_{14}A_1H_4(A_2)\,.
\end{aligned} \tag{III–3}$$

Ici on a introduit l'abréviation (III–4). La proba-