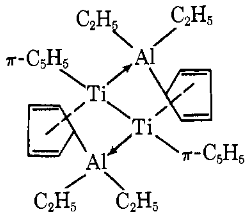
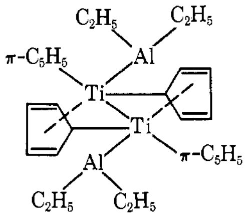
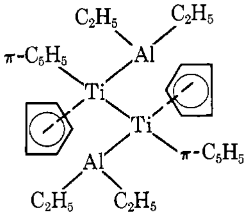


I



II



III

All three resonance forms are consistent with the diamagnetism of the compound. Forms I and II show clearly the half-bridge nature of the bonding between Ti and Al. Form I involves some Lewis basicity of the Ti atoms toward the Al atoms. This was suggested in the earlier study of this compound.[3] Recently, other examples of Lewis basicity of metals have been reported.[9–11]

The Crystal Structure

Figure 3 shows the content of the unit cell projected on the *bc* plane. Ethyl groups and cyclopentadienyl rings clustered about axes parallel to the *a* axis and containing centers of symmetry exhibit the closest packing distances. Minimum carbon–carbon distances of 3.52 A between centrosymmetrically related methyl groups and of 3.48 A for similarly related cyclopentadienyl rings are observed. No H–H contact distances less than 2.24 A have been calculated with the hydrogen atoms in the positions listed in Table II.

Acknowledgments.—The authors are grateful to Professor G. Paiaro, who furnished the compound, and to Dr. G. Diana and Mr. M. Perego for their cooperation in the first part of the work.

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(10) G. W. Parshall, *ibid.*, **86**, 361 (1964).

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X-Ray Analyses of the Structures of Two Crystalline Forms of *trans*-Dichlorotetrakis(ethylenethiourea)nickel(II)[1]

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trans-Dichlorotetrakis(ethylenethiourea)nickel(II), $Ni[SC(NHCH_2)_2]_4Cl_2$, is polymorphous, crystallizing in the triclinic system with one molecule in the unit cell (space group $P\bar{1}$) and in the monoclinic system with four molecules in the unit cell (space group C2/c). Both structures have the same NiS_4 skeleton, including two unequal independent Ni–S bonds, but differ in the orientation and length of the Ni–Cl bonds and also in the orientation of the ethylenethiourea ligands. There is no clear evidence for intermolecular or intramolecular hydrogen bonding in these crystals.

Introduction

The structure of dichlorotetrakis(ethylenethiourea)-nickel(II) $[Ni(etu)_4Cl_2]$ was first investigated by Nardelli, Chierici, and Braibanti.[3] Weissenberg photographs were obtained by rotating small yellow crystals about the *z* axis. Crystallographic data were reported as $a = 8.42$, $b = 8.44$, $c = 8.82$ A; $\alpha = 107.0°$, $\beta = 117.5°$, $\gamma = 90.2°$; $V = 524$ A^3; $Z = 1$; $D_m = 1.67$; $D_c = 1.70$. A qualitative comparison of *hk*0 Weissenberg photographs[4] from this crystal and from the corresponding thiourea complex,[5] $[Ni(tu)_4Cl_2]$, led these authors to deduce that there must be marked structural analogies between the compounds. In particular they concluded that the coordination of the four sulfur atoms of the ethylenethiourea molecules around the nickel atom must take place in one plane, chlorine atoms completing an octahedron in *trans* positions. This conclusion has, essentially, been confirmed by the present work.

Both yellow and orange crystalline forms of $[Ni(etu)_4Cl_2]$ were subsequently studied by Holt and Carlin.[6] The yellow form was assumed to be identical with the compound reported by Nardelli, *et al.*, and their conclusion that this was a *trans* complex was accepted. Indeed this conclusion was further supported by an examination of reflectance spectra. The splitting of spectral bands of the yellow compound was observed to be twice that of the orange compound, and it had been shown theoretically and experimentally

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(1) Research supported by Advanced Research Projects Agency Contract SD-86.

(2) To whom inquiries should be directed at the Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

(3) M. Nardelli, I. Chierici, and A. Braibanti, *Gazz. Chim. Ital.*, **88**, 37 (1958).

(4) M. Nardelli, private communication, 1966.

(5) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 942 (1956).

(6) S. L. Holt, Jr., and R. L. Carlin, *J. Am. Chem. Soc.*, **86**, 3017 (1964).

that such an effect would be produced if the compounds were *trans* and *cis* isomers, respectively. This paper describes complete X-ray structure analyses which have shown both crystalline forms to contain *trans* isomers only, thus contradicting the earlier conclusion.

Experimental Details and Crystallographic Data

Preparations of both crystalline forms of dichlorotetrakis-(ethylenethiourea)nickel(II), $Ni[SC(NHCH_2)_2]_4Cl_2$, have been detailed by Holt and Carlin.[6] The calculated formula weight is 538.3 and the linear absorpton coefficient, for Cu Kα radiation of wavelength 1.5418 A, is 70.1 cm^{-1}. Unit cell dimensions were obtained from single crystal Weissenberg and precession photographs taken at room temperature (20°) with this radiation. Maximum experimental errors in these quantities are indicated.

Orange Crystals.—These crystals were triclinic, space group $P\bar{1}$ determined by structure analysis, $a = 8.46 \pm 0.03$, $b = 8.41 \pm 0.03$, $c = 8.81 \pm 0.03$ A; $\alpha = 107.0 \pm 0.4°$, $\beta = 117.5 \pm 0.4°$, $\gamma = 90.5 \pm 0.2°$, $V = 524$ A^3; $D_m = 1.7$ g cm^{-3} (by flotation); $Z = 1$; $D_c = 1.70$ g cm^{-3}; $F(000) = 278$. These figures agree, within probable experimental error, with those given by Nardelli and co-workers[3] for what they described as yellow crystals.

Yellow Crystals.—These crystals were monoclinic, space group C2/c determined by structure analysis, $a = 17.57 \pm 0.07$, $b = 8.35 \pm 0.03$, $c = 16.74 \pm 0.07$ A; $\beta = 119.5 \pm 0.2°$; $V = 2128$ A^3; $D_m = 1.7$ g cm^{-3} (by flotation); $Z = 4$; $D_c = 1.68$ g cm^{-3}; $F(000) = 1112$. Thus the yellow crystals described as *trans*-$[Ni(etu)_4Cl_2]$ by Holt and Carlin were not the same yellow crystals also described as *trans*-$[Ni(etu)_4Cl_2]$ by Nardelli, *et al.*; because the subtle difference in color between the orange and yellow crystalline forms has led to confusion in the early work, they are henceforth distinguished as triclinic and monoclinic $[Ni(etu)_4Cl_2]$, respectively.

In both cases three-dimensional data were collected and mechanically integrated using a Nonius Weissenberg camera and Cu Kα radiation at room temperature. For the triclinic crystal the *h0l*, *hk0*, *hk1*, *hk2*, *hk3*, and *hk4* reciprocal lattice layers were recorded. In the monoclinic case only the *h0l*, *h1l*, *h2l*, *h3l*, and *h4l* layers were obtained by this method. The plateaus of all integrated spots, and adjacent background areas, were measured using a single-beam photometer and a galvanometer calibrated to read intensities directly. Small crystals (maximum dimensions ≤ 0.05 mm) were used and no absorption corrections applied. Structure factor magnitudes were derived from the relative intensities after the usual application of Lorentz-polarization corrections.

Structure Determinations

Space Groups.—For each crystal there existed two possible space groups; in the triclinic case P1 or $P\bar{1}$, and in the monoclinic case Cc or C2/c, the latter deduced from systematic absences among the X-ray spectra. In both cases the centrosymmetric alternatives required the heavy nickel atoms to be on special positions. Regardless of space group or isomeric form, the electron density distributions about the nickel atom would have been nearly centrosymmetric for the other heavy atoms (chlorine and sulfur). Conditions were hence not favorable for making conclusive distinctions between possible space groups by statistical methods. Until the contrary was proved, each structure was assumed to be noncentrosymmetric.

Computing.—Most of the calculations outlined in this paper were carried out on the Brown University IBM 7070 and System/360 Model 50 computers using programs written by the authors or modified by them to suit these facilities.

Three-dimensional least-squares refinements using the full-matrix program ORFLS[7] were also run on an IBM 7094 computer. With this program, refinements were carried out on $|F|$, the quantity $\Sigma w(F_o - S_qF)^2$ being minimized. Discrepancy indices were calculated as $R = \Sigma|F_o - S_qF|/\Sigma F_o$ and $R' = [\Sigma w(F_o - S_qF)^2/\Sigma w F_o^2]^{1/2}$. The scale factors S_q, used with each separately recorded Weissenberg layer, were allowed to vary but did not differ from each other by more than 10%. Values for R and R' quoted in this paper are, therefore, close to those which would be obtained using the more conventional definitions in which $S_q = 1$ and both sets of structure factors are on absolute scales. Structure factor tables in this paper are on absolute scales and were obtained by multiplying F values from ORFLS by S_q^{-1}.

In all these refinements use was made of the weighting scheme introduced by Hughes[8] in which $w \propto 1/|F_o|^2$ for $|F_o| > 4|F_{min}|$ and $w \propto {}^1/_{16}|F_{min}|^2$ for $|F_o| < 4|F_{min}|$. Scattering factors[9] for Ni^{2+}, Cl^-, S, N, and C, used in structure factor calculations, had real dispersion corrections applied for the heavy atoms only.

Interatomic distances and bond angles were calculated from atomic parameters using the program ORFFE.[10] Standard deviations in these functions include errors in the atomic parameters supplied to ORFFE in the form of the variance–covariance matrix obtained from the inverse matrix during the final cycle of least-squares refinement. Standard deviations in cell parameters, estimated as one-third of the maximum experimental errors quoted above, have also been included in these calculations.

Triclinic $[Ni(etu)_4Cl_2]$.—Projections of the sharpened Patterson function on (010) and (001) were constructed from 153 *h0l* reflections and 159 *hk0* reflections, respectively. Coordinates were derived for the heavy chlorine and sulfur atoms. Though indistinguishable, these primary ligands were clearly in distorted octahedral coordination about the nickel atom. Then 116 *h0l* reflections and 100 *hk0* reflections (*i.e.*, all the nonzero data) were used in two separate refinements of the heavy atom parameters. Initially all atoms were assigned isotropic temperature factors similar to those obtained by Lopez-Castro and Truter[11] for $[Ni(tu)_4Cl_2]$, and all ligands were designated as sulfur atoms. The resulting conventional R factors (observed reflections only) were 0.30 and 0.29 for the two sets of data. It was not possible to locate the light nitrogen and carbon atoms of the ethylenethiourea rings from difference Fourier projections.

Using the heavy atom parameters produced by the projection refinements, structure factor calculations for 822 measured *hkl* reflections gave an R factor of 0.33.

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(7) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(9) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1962, pp 202–205, 214.

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(11) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

TABLE I

STRUCTURAL PARAMETERS FOR TRICLINIC [$\mathrm{Ni(etu)_4Cl_2}$] WITH STANDARD DEVIATIONS[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	0.5	0.5	0.5	0.0088 (04)	0.0075 (03)	0.0109 (08)	0.0028 (03)	0.0055 (04)	0.0033 (04)
S(2)	0.5762 (03)	0.5291 (03)	0.8121 (04)	0.0116 (04)	0.0116 (04)	0.0125 (08)	0.0045 (03)	0.0058 (04)	0.0040 (05)
S(3)	0.3584 (03)	0.1981 (03)	0.3774 (04)	0.0133 (04)	0.0079 (03)	0.0155 (08)	0.0020 (03)	0.0087 (04)	0.0040 (04)
Cl(4)	0.7730 (03)	0.4010 (03)	0.5013 (04)	0.0104 (04)	0.0104 (04)	0.0159 (08)	0.0045 (03)	0.0083 (04)	0.0067 (04)
				B, A^2					
C(21)	0.7111 (12)	0.3952 (12)	0.8999 (16)	2.29 (20)					
N(22)	0.8160 (12)	0.3176 (12)	0.8364 (14)	3.85 (24)					
C(23)	0.9280 (13)	0.2232 (13)	0.9543 (16)	3.09 (24)					
C(24)	0.8485 (14)	0.2365 (15)	0.0856 (18)	3.96 (30)					
N(25)	0.7316 (12)	0.3595 (12)	0.0427 (15)	3.66 (24)					
C(31)	0.2896 (11)	0.1678 (11)	0.5188 (14)	2.02 (19)					
N(32)	0.1744 (10)	0.2491 (10)	0.5622 (13)	2.76 (20)					
C(33)	0.1501 (14)	0.1980 (14)	0.6951 (18)	3.60 (26)					
C(34)	0.2625 (14)	0.0543 (14)	0.7221 (17)	3.69 (28)					
N(35)	0.3314 (12)	0.0481 (12)	0.5932 (15)	4.20 (26)					

[a] The β values are the coefficients in the anisotropic temperature factor expression $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}l + 2\beta_{23}kl)\}$. The B values are the parameters in the isotropic temperature factor $\exp[-B(\sin\theta)^2/\lambda^2]$ for the light atoms; they were not varied during the final two cycles of refinement.

In the ensuing, inevitably centrosymmetric, three-dimensional difference maps, several of the highest peaks were in chemically sensible positions compatible with the established geometry of ethylenethiourea rings.[12] Two such rings were used, without their centrosymmetric equivalents, in a new structure factor calculation. This noncentric trial structure gave an R factor of 0.28 and the resulting difference maps clearly showed the other two ethylenethiourea rings in positions related to the first two by a center of symmetry at the nickel atom. One further structure factor calculation, using this centrosymmetric trial structure with chlorine and sulfur atoms now distinguished, gave an R factor of 0.14.

In three cycles of three-dimensional least-squares refinement varying 6 scale factors, 39 positional parameters, and 14 isotropic temperature parameters, values for the factors R and R', defined above, dropped to 0.086 and 0.118, respectively. Two further cycles of refinement varying the same scale factors and positional parameters as before but anisotropic temperature factors for the heavy atoms only gave final values for R and R' of 0.066 and 0.093, respectively. This represented no improvement over the penultimate structure factor calculation and the small shifts in all variable parameters confirmed that the refinement had converged. Maximum shifts as fractions of their estimated standard deviations in the final cycle of refinement were 0.16 for scale factors, 0.20 for positional parameters, and 0.68 for temperature factors. The final parameters are listed in Table I together with their estimated standard deviations.

In three-dimensional difference Fourier maps, calculated after the final structure factor calculation, the deviation in electron density, $\sigma(\rho) = (1/V)[\Sigma(\Delta F)^2]^{1/2}$, was 0.12 e/A^3. Several maxima in electron density were greater than 3σ, the largest value being 0.58 e/A^3. From interatomic distance calculations, five of these maxima could have represented hydrogen atoms but the others definitely could not. No attempt was made to refine these possible hydrogen atom positions or to include them in further structure analysis in any way.

Monoclinic [$\mathbf{Ni(etu)_4Cl_2}$].—Sections of a sharpened three-dimensional Patterson function over the asymmetric unit of space group C2/m were constructed from 513 *hkl* reflections. One of four equivalent nickel atoms in the unit cell was obviously on a center of symmetry at the origin if the correct space group was C2/c, or very close to the origin on a 2-fold rotation axis if the space group was Cc. Consideration of the shortest interatomic vectors established the orientation of the heavy ligand atoms in distorted octahedral configuration around this atom. A trial structure based on the noncentric space group led to a conventional R factor of 0.33 for 376 measured *hkl* reflections. Each light atom was independently resolved in subsequent difference Fourier syntheses. As in the triclinic case it was apparent, within experimental error, that the nickel atom was at the center of symmetry of a *trans* molecule. Structure factor calculations in space group C2/c with chlorine and sulfur atoms distinguished gave an R factor of 0.13.

In three cycles of three-dimensional least-squares refinement varying 5 scale factors, 39 positional parameters, and 14 isotropic temperature parameters, values for the factors R and R' were reduced to 0.095 and 0.110, respectively. Isotropic temperature factors were then converted to anisotropic form but refinement ceased when some temperature factor coefficients were no longer positive-definite. The correlation matrix showed serious interactions between β_{12}, β_{22}, β_{23} and the scale factors for each Weissenberg reciprocal lattice layer of constant k. This was understandable since these layers were only recorded up to $k = 4$ and no correlation data had been measured. Accordingly these anisotropic temperature coefficients were fixed at their equivalent isotropic values. Two cycles of anisotropic refinement then reduced values of R and R' to 0.088 and 0.104, respectively. By the same criteria as had

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(12) P. J. Wheatley, *Acta Cryst.*, **6**, 369 (1953).

Table II

Structural Parameters for Monoclinic [Ni(etu)$_4$Cl$_2$] with Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	0.5	0.5	0.5	0.0023 (03)	0.0057	0.0015 (03)	0.	0.0010 (02)	0.
S(2)	0.5403 (04)	0.5894 (09)	0.6574 (04)	0.0032 (03)	0.0081	0.0020 (04)	0.	0.0013 (03)	0.
S(3)	0.5165 (04)	0.2173 (09)	0.5430 (04)	0.0037 (04)	0.0092	0.0033 (04)	0.	0.0023 (03)	0.
Cl(4)	0.6473 (03)	0.4507 (08)	0.5168 (03)	0.0024 (03)	0.0065	0.0013 (03)	0.	0.0008 (03)	0.
				B, A^2					
C(21)	0.6396 (12)	0.5293 (26)	0.7375 (13)	0.82 (53)					
N(22)	0.7044 (10)	0.4746 (22)	0.7267 (11)	2.07 (46)					
C(23)	0.7880 (14)	0.4385 (31)	0.8126 (15)	2.65 (57)					
C(24)	0.7679 (14)	0.5098 (29)	0.8902 (14)	2.50 (57)					
N(25)	0.6724 (12)	0.5634 (28)	0.8289 (12)	3.36 (51)					
C(31)	0.4567 (13)	0.1443 (34)	0.5915 (13)	1.69 (57)					
N(32)	0.4026 (11)	0.2392 (25)	0.6085 (12)	2.36 (49)					
C(33)	0.3647 (15)	0.1356 (32)	0.6587 (16)	3.11 (61)					
C(34)	0.3894 (15)	0.9652 (39)	0.6430 (16)	3.86 (62)					
N(35)	0.4595 (12)	0.9976 (30)	0.6179 (12)	3.08 (50)					

[a] The β values are the coefficients in the anisotropic temperature factor expression $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. The B values are the parameters in the isotropic temperature factor $\exp[-B(\sin\theta)^2/\lambda^2]$ for the light atoms; they were not varied during the final two cycles of refinement.

been applied in the triclinic case, this refinement was considered to have converged. Maximum shifts as fractions of their estimated standard deviations in the final cycles of refinement were 0.07 for scale factors, 0.07 for positional parameters, and 2.07 for the isotropic temperature factor of the light carbon atom (34). Final parameters are listed in Table II together with their estimated standard deviations.

Futile attempts to locate hydrogen atoms, similar to those described for the triclinic structure, were made using final three-dimensional difference Fourier maps in which the standard deviation in electron density was 0.18 e/A^3 and the highest peak 0.67 e/A^3.

Observed structure factors and those calculated from the final parameters are compared in Tables III and IV for triclinic and monoclinic [Ni(etu)$_4$Cl$_2$], respectively. The inaccurate and unmeasured reflections listed in Table IV were obscured to varying degrees by the beam stop; they were not used in the refinement.

Description and Discussion of the Structures

In both crystalline forms of [Ni(etu)$_4$Cl$_2$] the nickel atoms lie on crystallographic centers of symmetry, so the individual molecules are necessarily *trans* complexes with three crystallographically independent ligands. One molecule from each structure is shown in Figure 1 projected normally onto the plane of its sulfur atoms. In both cases the light atoms attached to sulfur atom S(2) have been designated (21), (22), ... (25), and similarly for those attached to S(3). (This numbering does not necessarily imply structural similarity between like-numbered atoms.) The structures are shown also in Figure 2 in the form of stereoscopic pairs, viewed approximately at right angles to the view of Figure 1. Table V presents the more important interatomic distances and bond angles in the two structures, with estimated standard deviations in the least significant figures given in parentheses; the standard deviations include contributions from the errors in cell dimensions. Superscript primes have been used to distinguish equivalent atoms related by the center of symmetry at the nickel atom. The shortest intermolecular contacts are listed in Table V and shown in Figure 2. There are no other atoms within 3.5 A of the atoms in the central molecules in Figure 2.

The primary ligand atoms are arranged in approximate octahedral geometry about the nickel atom in both crystalline forms of [Ni(etu)$_4$Cl$_2$], but significant distortions from the ideal structure are evident. In each form there are two significantly different (difference greater than 3σ) Ni–S bond lengths, one about 2.45 A and the other about 2.49 A. The Ni–Cl bond also differs significantly in the two forms. The bond angles about the nickel atom deviate from right angles by significant amounts, and in the same general way in both forms, *i.e.*, all three bond angles involving Ni, Cl, S(2′), and S(3) are acute in the triclinic form, all those involving Ni, Cl, S(3), and S(2′) are acute in the monoclinic form. Qualitatively, these features demonstrate differences in the ligand fields at the central nickel atom of these complexes, as well as distortions from an octahedral field which must account for their different reflectance spectra.[6] Although the polymorphism found for [Ni(etu)$_4$Cl$_2$] is probably unusual for this type of compound, it is suggested that recent interpretations of ultraviolet–visible spectra[13] as indicating the presence of *cis–trans* isomers or *trans*-tetragonal structures for octahedral nickel(II) complexes should be accepted with caution. *trans*-[Ni(etu)$_4$Cl$_2$] does not approach tetragonal symmetry in either crystalline form.

Similar gross distortions from octahedral symmetry, and unequal Ni–S bond lengths, have recently been reported[14] for bis(thiourea)nickel(II) thiocyanate. In this compound the two Ni–S bonds (2.531 and 2.564 A) are longer than those in [Ni(etu)$_4$Cl$_2$] but the angle between them is smaller (83.6°), leading to the same shortest S···S contacts in all three molecules (3.39 ± 0.1 A).

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[13] J. Sirola and R. Ragsdale, *Inorg. Chem.*, **4**, 760 (1965); N. Curtis and Y. Curtis, *ibid.*, **4**, 804 (1965); M. Farago and J. James, *Chem. Commun.*, 470 (1965).

[14] M. Nardelli, G. Gasparri, G. Battistini, and P. Domiano, *Acta Cryst.*, **20**, 349 (1966).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TRICLINIC [Ni(etu)$_4$Cl$_2$]

H	K	OBS	CALC
L= 0			
1	0	426	-438
2	0	543	-506
3	0	176	-169
4	0	107	108
5	0	45	29
5	0	*	29
6	0	*	15
7	0	84	-74
8	0	*	35
9	0	*	-11
0	1	523	-582
1	1	318	328
-1	1	361	355
2	1	203	217
-2	1	542	-553
3	1	168	171
-3	1	583	632
4	1	305	-324
-4	1	251	-248
5	1	155	145
-5	1	300	-296
6	1	74	87
-6	1	127	114
7	1	*	-21
-7	1	*	59
8	1	*	-22
-8	1	*	9
9	1	*	-42
-9	1	*	8
0	2	*	22
1	2	993	-1264
-1	2	204	255
2	2	341	349
-2	2	211	237
3	2	229	232
-3	2	463	-524
4	2	209	228
-4	2	386	403
5	2	*	-60
-5	2	62	-50
6	2	167	-160
-6	2	*	-47
7	2	*	54
-7	2	*	-6
8	2	*	55
-8	2	*	-60
-9	2	92	87
0	3	365	-337
1	3	576	619
-1	3	125	140
2	3	304	-329
-2	3	471	-473
3	3	196	-181
-3	3	337	341
4	3	62	74
-4	3	172	153
5	3	*	17
-5	3	60	73
6	3	*	28
-6	3	210	-197
7	3	*	4
-7	3	*	53
8	3	77	-77
-8	3	*	67
-9	3	*	-23
0	4	228	236
1	4	119	-109
-1	4	303	-309
2	4	175	165
-2	4	583	623
3	4	*	44
-3	4	429	-418
4	4	166	-153
-4	4	89	-76
5	4	147	-134
-5	4	110	94
6	4	92	94
-6	4	149	135
7	4	*	13
-7	4	*	-17
8	4	*	19
-8	4	104	-79
-9	4	57	-62
0	5	192	193
1	5	*	1
-1	5	332	305
2	5	221	-224
-2	5	513	-495
3	5	150	164
-3	5	253	244
4	5	*	12
-4	5	208	-196
5	5	*	12
-5	5	143	139
6	5	*	-15
-6	5	74	-62
7	5	*	-51
-7	5	97	-104
-8	5	102	89
-9	5	*	35
0	6	67	74
1	6	198	-196
-1	6	229	-229
2	6	223	215
-2	6	172	159
3	6	*	-5
-3	6	*	2
4	6	100	-91
-4	6	130	110
5	6	90	86
-5	6	369	-335
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-7	1	299	285
-7	-1	184	184
-8	1	87	72
-8	-1	257	-252
-9	1	201	-186
-9	-1	*	-43
0	2	239	239
0	-2	253	290
1	2	86	-88
1	-2	143	-137
-1	2	70	-53
-1	-2	435	-477
2	2	145	-134
2	-2	115	120
-2	2	158	210
-2	-2	72	97
3	2	108	96
3	-2	85	-85
-3	2	507	-516
-3	-2	39	26
4	2	*	23
4	-2	101	-108
-4	2	135	102
-4	-2	277	261
5	2	*	-13
5	-2	184	187
-5	2	49	36
-5	-2	394	-407
6	-2	36	44
-6	2	162	165
-6	-2	107	108
-7	2	297	-287
-7	-2	*	-34
-8	2	116	104
-8	-2	88	90
-9	2	*	40
-9	-2	90	78
0	3	58	54
0	-3	143	-155
1	3	*	23
1	-3	*	23
-1	3	*	-36
-1	-3	253	233
2	3	*	45
2	-3	126	-138
-2	3	321	-369
-2	-3	137	-140
3	3	57	-92
3	-3	173	167
-3	3	388	384
-3	-3	383	366
4	3	80	-76
4	-3	88	81
-4	3	159	-160
-4	-3	440	-441
5	-3	*	-17
-5	3	156	154
-5	-3	194	196
6	-3	40	-49
-6	3	208	-187
-6	-3	*	-57
-7	3	84	83
-7	-3	154	-156
-8	3	93	79
-8	-3	*	33
-9	3	*	50
-9	-3	71	66
0	4	137	-136
0	-4	166	152
1	4	96	-100
1	-4	*	-4
-1	4	63	66
-1	-4	325	-351
2	4	71	63
2	-4	143	116
-2	4	201	200
-2	-4	495	493
3	-4	*	-16
-3	4	134	-144
-3	-4	251	-231
4	-4	85	-113
-4	4	155	153
-4	-4	117	106
5	-4	*	-45
-5	4	278	-280
-5	-4	116	-112
6	-4	89	96
-6	4	339	352
-6	-4	*	-33
-7	4	58	-60
-7	-4	123	111
-8	4	95	-99
-8	-4	*	29
-9	4	*	-15
-9	-4	132	-136
0	5	*	-1
0	-5	200	-193
1	5	58	45
1	-5	250	248
-1	5	106	111
-1	-5	425	399
2	5	*	-30
2	-5	153	-152
-2	5	155	-143
-2	-5	354	-348
3	-5	144	-134
-3	5	*	10
-3	-5	77	-59
4	-5	60	62
-4	5	54	60
-4	-5	60	70
5	-5	*	26
-5	5	231	222
-5	-5	198	185
-6	5	326	-315
-6	-5	72	-69
-7	5	77	90
-7	-5	*	36
-8	5	*	-68
-8	-5	*	-34
0	6	*	-33
1	6	95	112
-1	6	118	-111
-1	-6	152	-144
2	-6	242	256
-2	6	132	132
-2	-6	126	117
3	-6	*	6
-3	6	100	-94
-3	-6	72	-74
4	-6	*	-33
-4	6	91	101
-4	-6	110	111
5	-6	*	-40
-5	6	151	-166
-5	-6	181	-185
-6	6	81	37
-6	-6	146	149
-7	6	*	0
-7	-6	69	74
0	7	62	64
-1	7	*	23
-1	-7	90	73
-2	7	*	4
-2	-7	306	-302
-3	7	*	-35
-3	-7	313	307
-4	7	201	-207
-4	-7	*	-24
-5	7	245	256
-5	-7	98	-97
-6	-7	*	-20
-7	7	*	-3
-7	-7	*	-44
-2	-8	223	219
-3	-8	83	-77
-5	-8	70	67
H	L	OBS	CALC
K= 0			
0	5	109	-85
1	5	95	106
-1	5	312	-341
2	5	*	7
-2	5	251	251
3	5	123	125
-3	5	335	328
4	5	183	-205
-4	5	319	-347
5	5	59	56
-5	5	293	281
-6	5	65	-57
-7	5	75	80
-8	5	202	-186
-9	5	44	23
-10	5	57	-44
0	6	208	195
1	6	200	-224
-1	6	*	8
2	6	112	107
-2	6	*	-37
3	6	154	-177
-3	6	*	-17
4	6	77	92
-4	6	146	152
-5	6	*	-10
-6	6	75	-6
-7	6	112	-108
-8	6	*	48
-9	6	63	67
-10	6	37	43
0	7	197	-190
1	7	130	123
-1	7	84	94
2	7	*	-20
-2	7	*	-3
3	7	35	-49
-3	7	153	145
-4	7	248	-248
-5	7	134	133
-6	7	*	18
-7	7	168	158
-8	7	104	-85
-9	7	152	-142
-10	7	74	70
0	8	56	52
1	8	*	-23
-1	8	53	-64
2	8	*	-55
-2	8	*	-24
-3	8	55	84
-4	8	85	92
-5	8	124	-108
-6	8	161	131
-7	8	266	-237
-8	8	187	179
-9	8	*	16
0	9	114	-134
-1	9	67	68
-2	9	79	64
-3	9	*	9
-4	9	*	-26
-5	9	162	-127
-6	9	90	87
-7	9	177	170
-8	9	161	-161
-3	10	79	-88
-4	10	85	94
-5	10	38	40
-6	10	73	-66
-7	10	*	-28

* UNMEASURED REFLECTIONS

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR MONOCLINIC [Ni(etu)$_4$Cl$_2$]

H	L	OBS	CALC
K= 0			
4	0	89	91
6	0	166	205
8	0	97	103
10	0	*	-30
12	0	*	-33
0	2	136	140
2	2	239	262
-2	2	137	143
4	2	114	89
-4	2	60	62
6	2	*	26
-6	2	237	294
8	2	96	86
-8	2	170	193
10	2	58	-37
-10	2	69	82
-12	2	79	79
0	4	*	28
2	4	41	-47
-2	4	*	-3
4	4	65	66
-4	4	73	-74
6	4	242	238
-6	4	106	111
8	4	59	54
-8	4	174	194
-10	4	54	59
-12	4	107	101
-14	4	204	213
0	6	217	198
2	6	63	-50
-2	6	249	252
4	6	*	14
-4	6	*	12
6	6	119	105
-6	6	184	173
8	6	*	1
-8	6	131	124
-10	6	46	47
-12	6	53	62
-14	6	83	66
0	8	126	121
2	8	*	-26
-2	8	112	97
4	8	124	-114
-4	8	122	112
-6	8	140	128
-8	8	248	252
-10	8	54	52
-12	8	*	48
-14	8	97	92
0	10	*	0
2	10	108	-94
-2	10	*	26
-4	10	102	-101
-6	10	58	-55
-8	10	97	88
-10	10	58	50
-12	10	*	22
-2	12	*	40
-4	12	81	-89
-6	12	*	-36
-8	12	*	-4
-10	12	*	-49
-12	12	83	-76
K= 1			
3	0	36	-64
5	0	97	103
7	0	138	149
9	0	47	-41
11	0	*	3
1	1	16	-23
-1	1	63	-23
3	1	31	32
-3	1	18	-33
5	1	56	53
-5	1	*	-5
7	1	57	-53
-7	1	*	19
9	1	67	-70
-9	1	*	13
11	1	*	-29
-11	1	*	-5
1	2	46	31
3	2	181	-187
-3	2	195	198
5	2	49	-36
-5	2	60	68
7	2	63	57
-7	2	182	206
9	2	*	-21
-9	2	99	125
11	2	*	1
-11	2	97	57
-13	2	69	57
1	3	216	-200
-1	3	80	-67
3	3	123	-125
-3	3	52	46
5	3	55	-53
-5	3	23	23
7	3	71	-71
-7	3	*	17
9	3	82	-81
-9	3	55	55
-11	3	18	26
-13	3	*	-1
1	4	154	153
-1	4	221	212
3	4	47	-41
-3	4	146	-147
5	4	120	105
-5	4	30	-29
7	4	94	97
-7	4	125	136
9	4	65	66
-9	4	53	51
-11	4	65	-65
-13	4	75	80
1	5	175	-160
-1	5	106	-97
3	5	124	-128
-3	5	54	-55
5	5	52	-66
-5	5	83	-125
7	5	30	-27
-7	5	38	-31
-9	5	*	8
-11	5	*	4
-13	5	36	35
1	6	127	120
-1	6	232	219
3	6	136	129
-3	6	44	39
5	6	137	137
-5	6	28	8
7	6	107	89
-7	6	56	58
-9	6	58	-54
-11	6	63	-58
-13	6	*	9
1	7	28	-21
-1	7	*	-15
3	7	*	-9
-3	7	64	-57
5	7	*	0
-5	7	109	-104
-7	7	143	-136
-9	7	53	-58
-11	7	45	-42
1	8	37	37
-1	8	114	113
3	8	51	-49
-3	8	48	55
5	8	53	49
-5	8	61	66
-7	8	101	106
-9	8	142	149
-11	8	*	-8
-13	8	62	58
1	9	*	-21
-1	9	*	-13
3	9	*	14
-3	9	*	-8
-5	9	56	-55
-7	9	49	-47
-9	9	*	-22
-11	9	61	-55
-13	9	102	-104
1	10	59	-53
-1	10	103	99
3	10	*	-4
-3	10	*	8
-5	10	95	-81
-7	10	147	144
-9	10	98	88
-11	10	68	75
-13	10	47	48
1	11	43	-44
-1	11	39	-61
-3	11	*	-32
-5	11	48	-53
-7	11	*	-38
-9	11	*	-15
-11	11	48	-51
-13	11	25	-29
-1	12	74	87
-3	12	60	72
-5	12	*	7
-7	12	64	70
-9	12	41	41
-11	12	57	-56
-5	13	*	-12
-7	13	49	-65
-9	13	57	-64
K= 2			
2	0	77	-88
4	0	*	-8
6	0	89	94
8	0	*	23
10	0	43	-52
2	1	26	26
-2	1	149	179
4	1	105	86
-4	1	78	-78
6	1	96	93
-6	1	31	-32
8	1	*	-17
-8	1	*	0
10	1	33	-34
-10	1	72	-80
-12	1	76	-71
0	2	43	-37
2	2	*	-14
-2	2	49	47
4	2	*	-15
-4	2	72	-69
6	2	38	42
-6	2	47	50
8	2	86	92
-8	2	*	9
10	2	31	-27
-10	2	*	-21
-12	2	26	20
0	3	71	66
2	3	*	11
-2	3	84	95
4	3	*	2
-4	3	160	160
6	3	*	-12
-6	3	*	9
8	3	71	-65
-8	3	42	46
10	3	*	-7
-10	3	21	28
-12	3	51	-49
0	4	82	87
2	4	35	-33
-2	4	*	-8
4	4	28	-28
-4	4	131	-140
6	4	161	148
-6	4	*	-15
8	4	63	70
-8	4	35	41
-10	4	24	-26
-12	4	*	8
0	5	101	-86
2	5	51	-46
-2	5	56	44
4	5	92	89
-4	5	77	-71
6	5	29	19
-6	5	65	-70
8	5	25	24
-8	5	36	31
-10	5	61	65
-12	5	*	6
0	6	174	158
2	6	48	49
-2	6	163	148
4	6	80	67
-4	6	52	-56
6	6	104	96
-6	6	60	59
-8	6	57	55
-10	6	*	-3
-12	6	*	-17
0	7	26	24
2	7	38	36
-2	7	84	68
4	7	97	90
-4	7	41	-20
6	7	78	75
-6	7	72	-76
-8	7	*	-1
-10	7	*	-5
-12	7	36	-32
0	8	140	147
2	8	74	73
-2	8	88	77
4	8	38	38
-4	8	80	76
-6	8	88	85
-8	8	174	171
-10	8	36	-29
-12	8	41	-45
0	9	*	9
2	9	*	-4
-2	9	61	57
-4	9	112	114
-6	9	61	58
-8	9	70	57
-10	9	46	61
-12	9	*	-7
0	10	71	72
2	10	*	-8
-2	10	102	106
-4	10	21	29
-6	10	46	46
-8	10	79	84
-10	10	*	18
-12	10	*	8
0	11	95	-87
-2	11	*	19
-4	11	12	26
-6	11	*	-21
-8	11	45	50
-10	11	95	104
-12	11	42	47
-2	12	107	118
-4	12	38	37
-6	12	55	52
-8	12	60	66
-10	12	58	51
-6	13	53	-54
-8	13	36	-34
K= 3			
3	0	*	1
5	0	94	95
7	0	135	140
9	0	*	32
11	0	*	25
1	1	53	56
3	1	32	31
-3	1	27	26
5	1	134	151
-5	1	111	-119
7	1	61	60
-7	1	62	-78
9	1	*	11
-9	1	50	-42
-11	1	85	-76
1	2	147	153
3	2	70	73
-3	2	136	154
5	2	78	73
-5	2	74	69
7	2	82	79
-7	2	119	125
9	2	*	27
-9	2	47	47
-11	2	60	56
1	3	*	2
-1	3	97	112
3	3	*	22
-3	3	111	117
5	3	*	15
-5	3	*	18
7	3	45	-47
-7	3	36	34
9	3	*	-31
-9	3	106	114
-11	3	*	12
1	4	122	115
-1	4	155	172
3	4	*	4
-3	4	66	47
5	4	93	94
-5	4	75	83
7	4	*	46
-7	4	116	124
-9	4	95	104
-11	4	*	4
1	5	70	-65
-1	5	*	-29
3	5	47	46
-3	5	41	40
5	5	67	67
-5	5	64	-70
7	5	*	11
-7	5	87	86
-9	5	94	97
-11	5	*	0
1	6	*	1
-1	6	103	107
3	6	*	23
-3	6	*	12
5	6	45	48
-5	6	50	39
-7	6	122	117
-9	6	75	75
-11	6	*	43
1	7	*	18
-1	7	86	85
3	7	79	84
-3	7	97	98
5	7	117	135
-5	7	43	36
-7	7	64	-60
-9	7	*	16
-11	7	*	-16
1	8	*	27
-1	8	50	46
3	8	*	-25
-3	8	*	11
-5	8	50	49
-7	8	77	70
-9	8	84	78
-11	8	*	26
1	9	*	-13
-1	9	76	84
-3	9	156	159
-5	9	84	71
-7	9	40	40
-9	9	86	77
-11	9	58	52
1	10	*	-19
-1	10	92	89
-3	10	73	64
-5	10	*	-14
-7	10	78	82
-9	10	64	56
-1	11	*	-44
-3	11	*	43
-5	11	*	-33
-7	11	*	0
-9	11	139	125
-5	12	*	-14
-7	12	63	55
K= 4			
2	0	48	42
4	0	68	59
6	0	72	68
8	0	89	92
10	0	68	75
0	1	*	4
2	1	12	-23
4	1	52	65
-4	1	62	-74
6	1	47	44
-6	1	*	-15
8	1	64	-67
-8	1	33	36
-10	1	35	-37
0	2	121	118
2	2	140	136
-2	2	106	104
4	2	127	134
-4	2	*	13
6	2	92	87
-6	2	72	74
8	2	62	64
-8	2	75	77
-10	2	39	39
0	3	79	-62
2	3	135	-132
-2	3	47	40
4	3	39	-34
-4	3	87	91
6	3	28	-24
-6	3	52	-56
8	3	84	-117
-8	3	53	60
-10	3	70	76
0	4	114	114
2	4	58	62
-2	4	105	89
4	4	*	7
-4	4	127	113
6	4	56	52
-6	4	182	188
-8	4	114	108
-10	4	41	40
0	5	125	-116
2	5	137	-130
-2	5	*	16
4	5	*	-2
-4	5	130	-117
6	5	42	-43
-6	5	82	-78
-8	5	33	35
-10	5	42	46
0	6	*	-6
2	6	*	-16
-2	6	104	105
4	6	*	3
-4	6	96	77
-6	6	110	90
-8	6	97	88
-10	6	88	82
0	7	39	-44
2	7	23	-5
-2	7	19	22
4	7	53	54
-4	7	52	-43
-6	7	128	-124
-8	7	58	-49
-10	7	*	-29
0	8	89	94
2	8	30	24
-2	8	34	31
-4	8	*	5
-6	8	36	-28
-8	8	56	52
-10	8	*	8
0	9	27	-34
-2	9	30	30
-4	9	36	44
-6	9	55	-51
-8	9	*	-21
-10	9	*	10
-2	10	47	44
-4	10	*	-1
-6	10	*	25
-8	10	36	39
-6	11	94	-89

INACCURATE & UNMEASURED LOW ANGLE REFLS.

20	0	138	217
11	0	25	161
-11	2	*	81
02	1	53	131
13	0	*	172
-13	1	65	191
-13	2	*	108
-24	1	56	90

* UNMEASURED REFLECTIONS

All these Ni–S bond lengths lie within the range 2.4–2.6 A reported[11,14] for six-coordinate nickel complexes. The different Ni–Cl bond lengths in both forms of [Ni(etu)$_4$Cl$_2$] also lie within the range established by earlier workers. In fact Lopez-Castro and Truter[11] found Ni–Cl bond lengths of 2.40 and 2.52 A within one molecule of [Ni(tu)$_4$Cl$_2$].

The Ni–Cl and Ni–S bond lengths were also calculated allowing for thermal motion using the methods of Busing and Levy.[15] When the lighter atom in each bonded pair was assumed to ride on the heavier atom, bonds increased in length by amounts less than their estimated standard deviations in Table V. When independent motion was assumed, bond lengths increased uniformly by 0.02 A. It is, therefore, considered unlikely that the significant differences in bond lengths to nickel noted above are the results of abnormal aniso-

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[15] W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

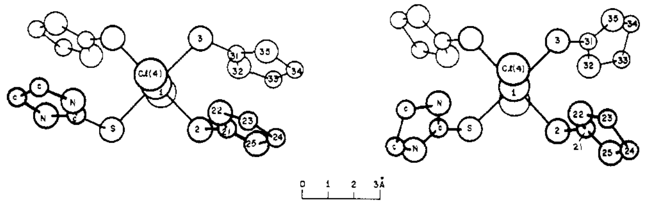

Figure 1.—Triclinic [Ni(etu)$_4$Cl$_2$] and monoclinic [Ni(etu)$_4$Cl$_2$] molecules projected normally onto planes defined by their sulfur atoms.

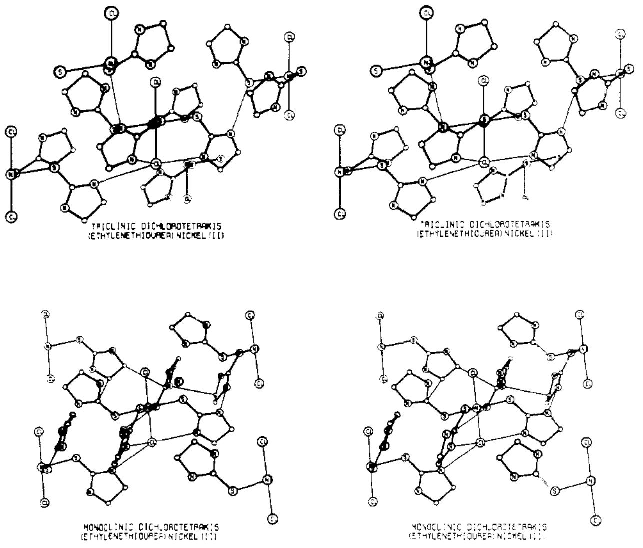

Figure 2.—Stereoscopic pairs showing one complete molecule from each structure together with nearest parts of neighboring molecules.

tropic thermal vibrations. The adjusted bond lengths are not tabulated because neither model provides an adequate description of the thermal motion, particularly of the sulfur atoms which are strongly bonded to two other atoms. It is also difficult to assign exact physical significance to anisotropic temperature factors in least-squares refinements where so many scale factors are variable parameters.

In each structure there are two crystallographically independent S–C bonds which are not significantly different in length although the shorter bond is always adjacent to the longer Ni–S bond. No individual S–C bond differs significantly in length from the figure given by Wheatley[12] for the free ligand (1.708 A).

Chemically equivalent bonds between light atoms of each structure have been groupd and averaged in Table V. In no case are there significant discrepancies within one group. For triclinic [Ni(etu)$_4$Cl$_2$] there is remarkably good agreement between the mean bond lengths and those given[12] for the free ligand (C(1)–N, 1.322 A; N–C(3,4), 1.471 A; C–C, 1.536 A). The general agreement is not so good in the monoclinic case, particularly for the mean N–C bond.

Unweighted least-squares planes were calculated for all of the ethylenethiourea groups and for the five-membered rings of carbon and nitrogen atoms included in these groups. In each case some atoms of the group lay 0.05 to 0.1 A off the plane and applications of the χ^2 test, as described by Wheatley[12] for ethylenethiourea, clearly demonstrated that none of the groups selected was statistically coplanar. Deviations from planarity were completely different for each ring, doubtless reflecting different environments in the crystals.

Table V

Interatomic Distances (A) and Bond Angles for [Ni(etu)$_4$Cl$_2$] with Estimated Standard Deviations in the Least Significant Figures

	Triclinic	Monoclinic
	Intramolecular	
Ni(1)–Cl(4)	2.457 (04)	2.496 (06)
–S(3)	2.490 (06)	2.443 (08)
–S(2)	2.451 (05)	2.482 (07)
S(2)–C(21)	1.698 (11)	1.669 (20)
S(3)–C(31)	1.677 (12)	1.724 (23)
Mean S–C	1.683 (08)	1.697 (15)
C(21)–N(22)	1.334 (14)	1.318 (22)
–N(25)	1.313 (14)	1.374 (23)
C(31)–N(32)	1.329 (12)	1.370 (25)
–N(35)	1.321 (15)	1.296 (26)
Mean C(-1)–N	1.324 (07)	1.340 (12)
N(22)–C(23)	1.480 (15)	1.495 (25)
N(25)–C(24)	1.447 (15)	1.541 (28)
N(32)–C(33)	1.454 (15)	1.566 (29)
N(35)–C(34)	1.488 (15)	1.511 (28)
Mean N–C(ethylene)	1.467 (08)	1.528 (14)
C(23)–C(24)	1.565 (17)	1.618 (30)
C(33)–C(34)	1.549 (15)	1.548 (35)
Mean C–C	1.557 (11)	1.583 (23)
S(2)···S(3)	3.602 (06)	3.564 (10)
···S(3′)	3.383 (06)	3.398 (10)
Cl(4)···S(2)	3.735 (07)	3.843 (08)
···S(3)	3.416 (08)	3.203 (09)
···S(2′)	3.183 (09)	3.163 (08)
···S(3′)	3.578 (06)	3.759 (09)
···N(22)	3.093 (12)	3.149 (17)
···N(32′)	3.218 (10)	3.171 (17)
S(2)–Ni(1)–S(3)	93.6° (0.3°)	92.7° (0.2°)
Cl(4)–Ni(1)–S(2)	99.1° (0.2°)	101.1° (0.2°)
Cl(4)–Ni(1)–S(3)	87.3° (0.2°)	80.9° (0.2°)
Ni(1)–S(2)–C(21)	115.0° (0.5°)	113.6° (0.7°)
Ni(1)–S(3)–C(31)	107.1° (0.3°)	117.9° (1.0°)
	Intermolecular	
S(2′)···N(25)	3.421 (11)	...
S(3′)···N(35)	3.318 (11)	...
Cl(4)···N(25)	...	3.383 (20)
S(3)···N(35′)	...	3.429 (20)

In each crystallographically independent ethylenethiourea ring there are two nitrogen atoms which could be involved in N–H···Cl or N–H···S hydrogen bonding. The six nonbonded interatomic distances to nitrogen in Table V are all less than the sum of the relevant van der Waals radii. All except the intramolecular Cl(4)···N(22) distance and the triclinic S···N distances can be ruled out as linear hydrogen bonds because of the chemically unlikely position in which hydrogen atoms would be located. A glance at Figure 1 will show that, in both structures, Cl(4) has adopted a position in which van der Waals repulsions from N(22), and the hydrogen atom attached to N(22), will be minimized. It seems unlikely that such large distortions from octahedral symmetry about the nickel atom are the result of attractive forces when explanatory repulsive forces are so obviously present. Repulsion explains the additional distortion in the monoclinic structure where the Cl(4)···N(32′) distance is also short (3.17 A). Also it appears, from the similarity of their ultraviolet–visible spectra,[6] that the two crystalline forms of $[Ni(etu)_4Br_2]$ are isostructural with the chlorine complexes; there halogen–nitrogen hydrogen bonds are less likely to exist.

The short S···N distances in the triclinic structure connect ethylenethiourea rings in different molecules which, though related by centers of symmetry, are not coplanar, being separated normally by about 0.5 A. The possibility of hydrogen bonding in this case cannot be ruled out although it seems unlikely.

In an independent infrared investigation one of us (S. L. H.) has found evidence that there is less hydrogen bonding in monoclinic $[Ni(etu)_4Cl_2]$, and more in triclinic $[Ni(etu)_4Cl_2]$, than in the free ligand. Wheatley, however, considered that there was no real evidence for N–H···S hydrogen bonds in the crystalline free ligand because there were other nonbonded interatomic distances that were abnormally short. This conclusion seems valid in the present work.

It is evident from Table V and the figures that the Ni–S–C bond angle is rather flexible and that an ethylenethiourea ligand can rotate easily about its S–C bond. Both factors help to explain why $[Ni(etu)_4Cl_2]$ molecules can form stable crystals with similar densities but different molecular environments.

Finally, it is to be noted that the nickel atom lies close (0.2 A) to the best least-squares planes through the individual ethylenethiourea ligands of monoclinic $[Ni(etu)_4Cl_2]$ but 0.8 to 2.0 A away from these planes in triclinic $[Ni(etu)_4Cl_2]$. Thus the geometry around the sulfur atoms does not indicate any special interaction of d orbitals on nickel and sulfur.

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The Rate of Displacement of H_2O in $Co(CN)_4(SO_3)OH_2^{3-}$ by CN^- and the Formation Quotient of $Co(CN)_4(SO_3)NH_3^{3-}$ from $Co(CN)_4(SO_3)OH^{4-}$ and NH_3[1]

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A kinetic study has been made of the rate of displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by CN^-. All experiments were at 25°, at unit ionic strength, and in the presence of a large excess of CN^-. In each experiment pseudo-first-order kinetic behavior was observed and characterized by a rate constant. The rate data are in agreement with a rate law given by

$$\frac{d \ln\{[Co(CN)_4(SO_3)OH_2^{3-}] + [Co(CN)_4(SO_3)OH^{4-}]\}}{dt} = \frac{1.73(CN^-)}{0.028 + (CN^-)}\,\frac{1}{1 + 776(OH^-)}$$

and are discussed in terms of a limiting type of SN1 mechanism. A numerical value of 98 ± 3 is reported for the equilibrium quotient for formation of $Co(CN)_4(SO_3)NH_3^{3-}$ by reaction of $Co(CN)_4(SO_3)OH^{4-}$ and NH_3.

Introduction

This paper is the first of a series dealing with the ligation reactions of $Co(CN)_4(SO_3)OH_2^{3-}$. In the present paper we report kinetic studies of the rate of displacement of H_2O in $Co(CN)_4(SO_3)OH_2^{3-}$ by CN^-, a process which occurs very rapidly by a limiting type of SN1 mechanism. In addition, a value is reported for the formation quotient of $Co(CN)_4(SO_3)NH_3^{3-}$, produced by the reaction of $Co(CN)_4(SO_3)OH^{4-}$ with aqueous NH_3.

The results are discussed in terms of the assumption that the SO_3^{2-} ligand has a remarkable *trans*-labilizing effect in Co(III) complexes. This assumption has been used to explain the results of earlier preparative studies[2,3] and, more recently, kinetic studies involving octahedral Co(III) complexes.[4,5]

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