Eine Bemerkung über K2[NiO2][1,2]*

Bernd Nowitzki und Rudolf Hoppe

Institut für Anorganische und Analytische Chemie der Justus-Liebig-Universität Giessen

K2[NiO2] wurde erneut in einkristalliner Form [Farbe der quaderförmingen Einkristalle: rot-violett/grün (Dichroismus)] durch Reaktion von überschüssigem $KO_{0,74}$ mit der Gefäßwand ('Ni-Bömbchen') bei der Darstellung von Oxogermanaten mit 'gemischten' Kationen des Typs $A_{4-x}A_x'GeO_4$ (A = Alkalimetall) erhalten (650 °C, 7d) und die Struktur verfeinert: 114 I_0(hkl), Vierkreisdiffraktometer PW 1100, ω-scan, MoK$_\alpha$, R = 4,46%, R_w = 3,60%, tetragonal, I 4/mmm, a = 395,28(13) c = 1283,84(65) pm, $d_{rö}$ = 2,79$_6$ g · cm^{-3}, Z = 2. Die Bindungsabstände und der Madelunganteil der Gitterenergie, MAPLE, wurden berechnet und diskutiert.

In connection with the preparation of oxogermanates with 'mixed' cations (typ: $A_{4-x}A_x'GeO_4$ with A = alkalimetals) single crystals [square shape, red-violet/green (dichroism)] of [K2NiO2] have been obtained anew by reaction of a surplus $KO_{0,74}$ with the sidewall of Ni-cylinders [650 °C, 7d].

The structure of K2[NiO2] has been refined: 114 I_0(hkl), four cycle diffractometer PW 1100, ω-scan, MoK$_\alpha$, R = 4,46%, R_w = = 3,60%, tetragonal, I 4/mmm, a = 395,28(13) c = 1283,84(65) pm, $d_{rö}$ = 2,79$_6$ g · cm^{-3}, Z = 2. The interatomic distances and the Madelung Part of Lattice Energy, MAPLE, are calculated and discussed.

Wie die Tabelle I zeigt, haben die der Zusammensetzung nach ähnlichen Oxide K2[BeO2][3], K2[ZnO2][4] und K2[NiO2] sehr unterschiedlichen Aufbau. Im ersten Fall liegen zweikernige Anionen vor, die charakteristische Koordinationszahl ist 3. Im Zincat liegen SiS2-analoge, unendliche Tetraederketten vor, und bei K2[NiO2] liegt, wie zuvor nur bei den Oxomercuraten A2[HgO2] mit A = Li—Cs[5] gefunden, eine 'aufgefüllte Molekülstruktur' des XeF2-Typs[6-8] vor. Rb2[NiO2] und Cs2[NiO2] schließen sich im Aufbau K2[NiO2] an[9].

Unerwartet ist nicht nur der Aufbau von K2[NiO2], sondern auch die Kürze des Abstandes d (Ni—O) = 1,68$_1$ Å.

Nun konnten wir seinerzeit nur Zweikreisdiffraktometerdaten auswerten. Da zudem der Madelunganteil der Gitterenergie, MAPLE, unbefriedigend mit

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TABELLE I

Motive der gegenseitigen Zuordnung bei $K_2[BeO_2]^3$, $K_2[ZnO_2]^4$ *und* $K_2[NiO_2]$

$K_4[Be_2O_4]$:

	$\overset{1}{1\ 0}$	$\overset{2}{1\ 0}$	C.N.
1 Be	1/1 + 1/1	1/1	3
$\overset{1}{1\ K}$	1/1 + 1/1	1/1	3
$\overset{2}{1\ K}$	1/1 + 1/1	1/1 + 1/1 + 1/1	5
C. N.	6	5	

$K_2[ZnO_2]$:

	2 0	C.N.
1 Zn	1/4	4
2 K	1/1 + 1/1 + 1/1 + 2/2	5
C. N.	6	

$K_2[NiO_2]$:

	2 0	C.N.
1 Ni	1/2	2
2 K	1/1 + 4/4	5
C. N.	6	

der Summe der MAPLE-Werte der binären Komponenten übereinstimmte ($\Delta = -1,9^0/_0$), erschien eine Verfeinerung der Struktur von $K_2[NiO_2]$ dringend geboten.

Vor längerer Zeit haben wir bei der Umsetzung von $Na[NiO_2]$ mit K_2O beobachtet, daß sich neben $K_3[Ni_2O_4]^{10}$ durch Reaktion mit der Wand des 'Ag--Bömbchens', aus dieser herauswachsend, schöne Einkristalle von $Na_3[AgO_2]^{11}$ bilden. Auch $KAgO^{12}$ konnte durch Reaktion von K_2O mit der Gefäßwand ('Ag-Bömbchen') in einkristalliner Form dargestellt werden[13]. In der Zwischenzeit haben wir festgestellt, daß es sich um eine Beobachtung handelt, die man bei vielen derartigen Austauschreaktionen und auch dann findent, wenn man z. B. 'überoxidiertes Kaliumoxid' (KO_x mit $x > 0,5$) schnell im z. B. 'Ni-Bömbchen' erhitzt (hier: z. B. Bildung von $K_2[NiO_2]^1$).

Die hier untersuchten Einkristalle entstanden bei Versuchen, die zur Darstellung von Oxogermanaten mit 'gemischten' Kationen des Typs $A_{4-x}A_x'GeO_4$ (A = Alkalimetall) vorgenommen wurden[14].

I. *Darstellung und Eigenschaften der Präparate*

Die Einkristalle wurden auf zwei verschiedenen Wegen erhalten:

a) Erhitzt man innige Gemenge von $KO_{0,74}$, $NaO_{0,50}$ und GeO_2 in verschlossenen 'Ni-Bömbchen', so entstand gemäß:

$$5KO_{0,74} + Na_{0,50} + GeO_2 + Ni = \text{'}K_3NaGeO_4\text{'} + K_2NiO_2 + \text{'}O, 1 O_2\text{'}$$
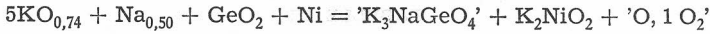
neben einem neuen Oxogermanat, mit dessen Untersuchung wir beschäftig sind, eine Reihe gut gewachsener Einkristalle von K_2NiO_2 (Ni-Bömbchen, Ni-Stopfen; 600—650 °C; 7d). Wichtig ist dabei die Aufheizrate, sie sollte bei 150 °C/h liegen.

b) Weniger gute Einkristalle entstanden auch dann, wenn man $KO_{1,88}$ (typischer Ansatz: 250 mg) im kleinen 'Ni-Bömbchen' analog tempert. Diese eigneten sich für die Datensammlung nicht.

Die quaderförmigen Einkristalle ($\varnothing$ = bis 0,4 mm) zeigten den bereits beschriebenen Dichroismus (rot-violett/grün). Ihre Beständigkeit gegen Luft ist gering, es trat sehr schnell Zersetzung unter Bildung einer zunächst schwarzen, später 'hellgrünen Substanz' ein.

II. Röntgenographische Untersuchungen

Die Gitterkonstanten wurden über Guinier-Sinon-Aufnahmen (CuK_α-Strahlung, Eichung mit T-Quarz: $a = 491,304$ $c = 540,463$ pm), vgl. Tabelle II, erneut bestimmt:

$$a = 395,28(13) \quad c = 1283,84(65) \text{ pm} \quad c/a = 3,24_8$$

Sie stimmen mit unseren älteren Werten ($a = 395,_3$ $c = 1285,_3$ pm)[2] gut überein.

Die Einkristalle wurden unter mit Na-Draht getrocknetem Paraffinöl mithilfe eines Polarisationsmikroskopes ausgesucht und mit üblichen Filmmethoden (Drehkristall-(hier um [100])und Weissenberg-(Okl, 1kl) Aufnahmen) voruntersucht. Der geeignetste (Nr. 3) wurde für die Datensammlung auf dem Vierkreisdiffraktometer verwendet.

TABELLE II

Auswertung einer Guinier-Simon-Aufnahme von $K_2[NiO_2]/(\text{'}K_3NaGeO_4\text{'})$ [+), diese Reflexe von K_2NiO_2 fallen mit Reflexen von 'K_3NaGeO_4' zusammen], CuK_α-Strahlung ($\lambda = 154,178$ pm), Eichung mit T-Quarz ($a = 491,304$ $c = 540,463$ pm)

h	k	l	$10^5 \sin^2 \Theta_o$	$10^5 \sin^2 \Theta_c$	I_o	I_c
0	0	2	1452	1442	0,5	54,4
1	0	1	4171	4164	1[+)	175,7
0	0	4	5793	5769	2[+)	30,6
1	0	3	7066	7048	10[+)	918,6
1	1	0	7615	7607	6	1000,0
1	1	2	—	9049	—	22,5
1	0	5	—	12817	—	12,1
0	0	6	12960	12980	2[+)	151,7
1	1	4	13415	13376	1[+)	28,8
2	0	0	15198	15214	3	348,0
2	0	2	—	16656	—	9,8
2	1	1	19381	19378	0,5	34,0
1	1	6	20578	20586	2	293,0
2	0	4	20968	20982	1[+)	12,1
1	0	7	—	21470	—	4,3

TABELLE III

K_2NiO_2 — *Kristallographische und röntgenographische Daten*

Kristallsystem	tetragonal
Raumgruppe	I 4/mmm — D_{4h}^{17}
Gitterkonstanten (Guinier-Simon-Daten, pm)	$a = 395,28(13)$ $c = 1283,84(65)$
Kristallform, -farbe, -größe	quaderförmig, rot-violett/grün (Dichroismus), $\varnothing = 0,4$ mm
Dichte (röntgenographisch, g/cm³)	$2,79_6$
Zahl der Formeleinheiten pro Elementarzelle	2
Molvolumen (röntgenographisch, cm³/Mol)	$60,40_5$
Molvolumen (Summe der binären Oxide, cm³/Mol)	51,05
F(000)	156,0
Linearer Absorptionskoeffizient (MoK_α, cm⁻¹)	54,50
Diffraktometer	Vierkreis (PW 1100)
Strahlung, Monochromator	MoK_α, Graphit
Korrekturen	Polarisations-, Lorentzfaktor
Meßbereich	$3° \leq \Theta \leq 30°$
Abtastung	ω-scan
Anzahl der symmetrieunabhängigen Reflexe	114
Löseverfahren	ref. 2
Parameterverfeinerung	'full-matrix' least squares, 'anisotrope' Temperaturfaktoren
Anzahl der freien Parameter	10
$R = \Sigma //F_o/ - /F_c// / \Sigma /F_o/$	0,0466
$R_w = \Sigma \sqrt{w} //F_o/ - /F_c// / \Sigma \sqrt{w}/F_o/$	0,0360

TABELLE IV

Lageparameter und 'anisotrope' Temperaturfaktoren von K_2NiO_2, Raumgruppe

I 4/mmm, (standardabweichungen in Einheiten der letzten Stelle in Klammern)

	Lage	x	y	z	U_{11}	U_{33}
Ni	2a	0	0	0	0,0129(45)	0,0163(11)
K	4e	0	0	0,6574(2)	0,0171(45)	0,0155(15)
O	4e	0	0	0,8686(6)	0,0172(50)	0,0183(29)

Der Temperaturfaktor (anisotrop) hat die Form:

$T_{aniso.} = \exp [-2 \pi^2 (2 U_{11} h^2 a^{*2} + U_{33} l^2 c^{*2})]$

TABELLE V

Interatomare Teilchenabstände bis 500 pm bei K_2NiO_2

	Ni	K	O
Ni	4x 395,3	8x 344,9	2x 168,7
		2x 439,8	8x 429,8
K	4x 344,9	4x 367,0	1x 271,1
	1x 439,8	4x 395,3	4x 281,5
		1x 404,2	4x 464,3
			4x 479,3
O	1x 168,7	1x 271,1	1x 337,4
	4x 429,8	4x 281,5	4x 395,3
		4x 464,3	4x 413,4
		4x 479,3	

Bezüglich der Einzelheiten der Untersuchung siehe Tabelle III. Tabelle IV gibt dioe Parameter nach dem Ende der Verfeinerung. In Tabelle V sind die wichtigsten Abstände zusammengestellt. Die Verfeinerung erfolgte, ausgehend von der bekannten Struktur, mithilfe von 'least-squares'-Methoden.

Der damals auffällig kurz erscheinende Abstand d(Ni-O) wird mit hier 1,687 Å (früher: 1,681 Å) prinzipiell bestätigt.

III. *Der Madelunganteil der Gitterenergie, MAPLE*[16]

Wir haben für K₂[NiO₂] MAPLE berechnet und mit den MAPLE-Werten der binären Oxide verglichen, siehe Tabelle VI. Diese zeigt:

TABELLE VI

Der Madelunganteil der Gitterenergie, MAPLE, von K_2NiO_2 in [kcal/Mol]

Teilchen	Faktor	binär	ternär		Δ ter.-bin.	
			'alt'[2]	'neu'[+]	'alt'[2]	'neu'[+]
Ni	1	556,4	504,0	501,3	—52,4	—55,1
K	2	104,9	118.7	119,0	27,6	28,2
O	1	556,4[a]	469,4	468,3	—87,0	—88,1
O	1	390,1[b]	469,4	468,3	79,3	78,2
K₂NiO₂	Σ	1712,7	1680,2	1675,9	—32,5	—36,8
					$\overset{\wedge}{=}$ —1,93%	$\overset{\wedge}{=}$ —2,20%

[a] aus NiO,   [b] aus K₂O,   [+] 'neu' = diese Arbeit

a) Die Diskrepanz zwischen der Summe der MAPLE-Werte der binären Oxide und MAPLE(K₂NiO₂) wird bestätigt, diese ist eher noch größer geworden.

b) Diese bemerkenswerte Abweichung geht ganz auf das Konto von Ni²⁺. So gesehen ist die Kürze des Abstandes d(Ni—O) noch immer nicht ausreichend, den Wechsel von der C.N. 6(NiO) zur C.N. 2 hier auszugleichen.

c) Der Paramagnetismus von K₂[NiO₂]² zeigt, daß der Verlust an MAPLE nicht durch zusätzliche Kovalenz unter Teilnahme der 3d-Orbitale von Ni²⁺ kompensiert

werden kann, was naturgemäß nicht ausschließt, daß über 4d-Orbitale zusätzlich eine (dann sicher schwächere) Kovalenz ermöglich wird.

d) Es ist bekannt, wie schwierig die Darstellung von formelreinen Präparaten von NiO ist[15]. Die Diskrepanz kann aber schwerlich durch die vermutlich nur geringe Unsicherheit bezüglich MAPLE(NiO) erklärt werden.

e) Eher schon könnte der gegenüber den Ausgangsoxiden sicherlich stärkere Einfluß des Entropiegliedes auf (ΔG^0_{298} bzw.) ΔG^0_{1000} entscheidend sein.

Beim jetzigen Stand unserer Kenntnisse könnte hier die Grenze des 'MAPLE--Konzeptes'[16] überschritten sein. So müßte ja wie sonst üblich gelten:

$$\text{MAPLE } (K_2NiO_2) = \text{MAPLE } (K_2O) + \text{MAPLE (NiO)}$$
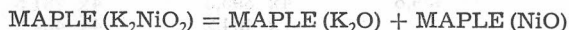
IV. DISKUSSION

Das Ergebnis dieser Überprüfung befriedigt und überrascht:

a) Befriedigend ist nicht nur die gute Übereinstimmung mit den Ergebnissen der älteren Untersuchung mit Zweikreisdiffraktometerdaten (alt: $R = 7,98^0/o$; diese Arbeit: $R = 4,66^0/o/d$ (Ni—O): alt: 1,68$_1$ Å; diese Arbeit: 1,68$_7$ Å).

Diese zeigt vielmehr, berücksichtigt man die Isotypie zu den Oxomercuraten, hier also insbesondere $K_2[HgO_2]$, daß eine tiefgehende Analogie über Schrägbeziehungen im Periodensystem der Elemente von Ni (über Ag?) zum Hg reicht.

b) Überrascht sind wir, daß die Diskrepanz der MAPLE-Werte bestätigt wird. Inzwischen haben wir nämlich $KNa_2[CuO_2]$[17] dargestellt. Auch hier liegt, was den $[CuO_2]$-Teil der Struktur anbelangt, eine 'aufgefüllte' Molekülstruktur vom XeF_2-Typ vor. Ähnlich wie bei $K_2[NiO_2]$ sind die Abstände d(Cu—O) in der 'Hantel' O—Cu—O kurz (1,73$_1$ Å bzw. 1,82$_4$ Å), aber die Übereinstimmung der MAPLE-Werte im Sinne des oben zitierten MAPLE-Konzeptes ist in diesem Fall ausgesprochen gut.

c) Aufregend sind die beim jetzigen Stand unserer Kenntnisse vorhandenen Strukturunterschiede zu den Oxoargentaten(I) der Alkalimetalle, nämlich $Na_3[AgO_2]$[11] bzw. $K_3[AgO_2]$[18]. Hier liegen, durch die Ergebnisse zweier Arbeitsgruppen unabhängig bestätigt, keine Derivate der XeF_2-Mutterstruktur vor, sondern Varianten vom 'Na$_2$O-bzw. K$_2$O-Typ' dergestalt, daß durch Hinausrücken von Ag+ aus den Tetraederlücken die 'Hanteln' O—Ag—O innerhalb des ansonsten zum Anti-CaF$_2$-Typs gehörenden Kolektivs gebildet werden.

d) Abschießend sei noch einmal auf die gravierenden Unterschiede der Kristallstrukturen, vgl. Tabelle I, so ähnlich zusammengesetzter und letzthin verwandter Verbindungen wie $K_2BeO_2 = K_4[Be_2O_4]$, $K_2[NiO_2]$ und $K_2ZnO_2 =$ hingewiesen und darauf, daß die Substitution von K+ durch Rb+ oder Cs+ bei $= K_2[ZnO_{4/2}]$ gemäß $A_8[Zn_4O_8] = A_8[OZn_2 ZnO_2 ZnO_2 ZnO]$ mit A = Rb, Cs zu einer weiteren Komplikation führt, in dem hier die Hälfte von Zn^{2+} die ungewöhnliche C. N. 3 gegenüber O^{2-} aufweist[19] und oligomere auftreten. Wir sind bei den vorliegenden Kenntnissen nicht imstande, diese Unterschiede auch nur halbwegs plausibel zu erklären.

V. SCHLUSSBEMERKUNG

Mit der Darstellung weiterer Oxonickelate(II), Versuchen zur Synthese neuer Oxocuprate(I), wie z. B. K_3CuO_2[20] und schließlich von Oxoargentaten, wie $KNa_2[AgO_2]$ sind wir beschäftigt. Vielleicht hängen die Diskrepanzen bezüglich

MAPLE doch mit den Unsicherheiten zusammen, die noch immer über formelreine Einkristalle von NiO bestehen.

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SAŽETAK

Neka zapažanja o K₂[NiO₂]

B. Nowitzki i R. Hoppe

Monokristali $K_2[NiO_2]$ (prizmatski, crveno-ljubičasti/zeleni, dihroizam) nastali su reakcijom viška $KO_{0,74}$ sa stijenkama niklene reakcijske posude za vrijeme pripreve (650 °C, 7d) oksogermanata »miješanih« kationa tipa $A_{4-x}A_x'GeO_4$ (A = alkalijski metal). Struktura je utočnjena na osnovi 114 refleksa, prikupljenih na četverokružnom difraktometru PW 1100 tehnikom ω-skaniranja uz MoKα zračenje, do $R = 4,46^0/o$ ($R_w = 3,60^0/o$). Kristali su tetragonski, prostorna grupa I4/mmm, dimenzija jedinične ćelije $a = 395,28(13)$, $c = 1283,84(35)$ pm, $D_x = 2,76_6$ g cm⁻³, Z = 2. Izračunani su i prodiskutirani međuatomski razmaci i Madelungov udio u energiji kristalne rešetke (MAPLE).

Structural Aspects of 2-Thioimidazolidine Coordination in Silver(I) Halide Complexes*

*Luigi P. Battaglia, Anna Bonamartini Corradi, and Mario Nardelli**

Istituto di Chimica Generale e Inorganica dell'Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C. N. R., via M. D'Azeglio 85, 43100 Parma, Italy

The crystal structures of AgCl · 2etu and AgBr · 2etu [etu = = 2-thioimidazolidine = ethylenethiourea = SC(NHCH$_2$)$_2$] have been determined and that of uncomplexed etu itself has been redetermined using MoKα diffractometer data. AgCl · 2etu: $P2_1/c$, $a = 11.078(4)$, $b = 14.046(6)$, $c = 7.749(2)$ Å, $\beta = 103.71(2)$, $Z = 4$, final R_F (1372) = $= 0.0558$. AgBr · 2etu: $P2_1/n$, $a = 9.050(1)$, $b = 10.557(3)$, $c = 13.191(4)$ Å, $\beta = 103,38(1)°$, $Z = 4$, final R_F (1976) = 0.0379. Etu: $P2_1/c$, $a = = 5.801(3)$, $b = 14.540(5)$, $c = 5.774(3)$ Å, $\beta = 101.3(1)°$, $Z = 4$, final R_F (506) = 0.0235. Metal coordination is distorted tetrahedral in both complexes, but the structure of AgCl · 2etu is polymeric with one etu ligand terminal [Ag—S = 2.512(3) Å] and one bridging through sulphur [Ag—S = 2.551(3), 2.655(4) Å], while the structure of AgBr · 2etu is built by centrosymmetric dimers with the two etu ligands terminal [Ag—S = 2.482(2), 2.489(2) Å] and bromine acting as a bridge [Ag—Br = 2.817(1), 2.847(1) Å]. Relevant parameters for uncomplexed etu are: S—C (sp^2) = 1.694(3), N—C (sp^2) = = 1.349(3) av., N—C (sp^3) = 1.460(3) av., C (sp^3)—C (sp^3) = 1.561(5) Å (values corrected for thermal motion), N—C—N = 108.4(2)°, C—N—C = 113.3(2)° av., N—C—C = 102.5(3)° av.. Metal coordination seems to influence the S—C—N angles: that on the side of the lone pair interacting with metal is always larger [126.6(3)° av.] than that on the other side [124.3(2)° av.], while the thioureic moiety of the ligand maintains its planarity. The librational thermal motion of ethylenethiourea in the crystals when uncomplexed and in silver-complexes is quite similar.

1. INTRODUCTION

It is well recognized that thiourea [SC(NH$_2$)$_2$ = tu] and ethylenethiourea [SC(NHCH$_2$)$_2$ = 2-thioimidazolidine = etu] behave as monodentate ligands through the sulphur atom which can coordinate to a single metal centre or, as a bridge, to adjacent metal atoms. No case has been found of crystal structures where the nitrogen atoms of the ligand are involved in coordination to metal. The interactions between sulphur and a metal centre are influenced by the nature of the other ligands and of the metal atom, and by the ratio metal/ligands.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.
** To whom correspondence should be addressed

Our research investigates these effects further. Two complexes formed by AgCl and AgBr with ethylenethiourea have been considered and a new accurate analysis of the crystal structure of ethylenethiourea itself has been carried out. In the present paper the results of crystal structure analyses of these compounds are reported and show that the two complexes exhibit quite different structures, even if their stoichiometry and metal coordination are the same. This could not be foreseen simply on the basis of the different size of the anions. Moreover, comparison with the uncomplexed ethylenethiourea shows that coordination to metal affects the S—C—N angles, the variations of the other structural parameters, if any, not being detectable with certainty at the level of the attained accuracy.

2. EXPERIMENTAL

Crystals of AgX · 2etu (X = Cl, Br) were obtained, together with crystals of AgX · 3etu, by slow cooling of hot aqueous solutions containing the silver halide and ethylenethiourea in excess, as described by Morgan and Burstall[1] for the preparation of AgCl · 3etu and AgBr · 2etu. The crystal of uncomplexed etu used for the structure analysis was from a commercial sample recrystallized from ethanol.

The relevant data concerning the crystal structure analyses are summarized in Table I. Crystal data and starting coordinates for the refinement of the etu crystal structure were taken from the analysis of Wheatley[2], assuming the standard P2₁/c orientation. The agreement index for merged reflections was $R = 0.0202$.

The intensity data of etu were not corrected for absorption, while two refinements were carried out for both silver complexes, one with no absorption correction[3], the other with the empirical correction for absorption and extinction proposed by Walker and Stuart[4]. This correction not only reduced the residuals (the conventional R index improved from 0.0630 to 0.0558 for AgCl · 2etu and from 0.0600 to 0.0379 for AgBr · 2etu), but also gave the following effects:

(a) in AgCl · 2etu:

— the differences between the S—C distances in the two ligands are reduced by 0.015 Å,

— the differences between the N—C (sp²) distances are reduced by 0.023 Å both in each ligand and in the two ligands,

— the N—H distances increase by 0.06 Å av., and the difference between the maximum and minimum value decreases from 0.22 to 0.17 Å,

— the average C—H distance practically does not change, but the difference between the minimum and maximum value reduces from 0.50 to 0.45 Å,

— on average, the isotropic equivalent thermal parameters show a 10% increase and the anisotropy, as indicated by the ratio between the maximum and minimum values of the mean squares displacements of the thermal ellipsoids, is reduced by 12%.

(b) in AgBr · 2etu:

— the S—C distances practically do not change,

— the average of the N—C (sp²) distances decreases becoming equal to the same average for AgCl · 2etu, and the same can be said for the N—H distances,

— also, the mean C—H distance becomes equal to the same mean for AgCl · 2etu,

— on average, the isotropic equivalent thermal parameters do not change, while the anisotropy reduces by 20%.

For both complexes the absorption correction gave no significant variation in distances and angles involving the heaviest atoms.

All the structures were refined by full-matrix least-squares using the SHELX-76 program[5]. The hydrogen atoms were located from difference Fourier syntheses and refined isotropically for the two metal-complexes and anisotropically for the uncomplexed etu. The 040 reflection was omitted in the refinement of the last compound as its intensity appeared to be affected by measurement errors. The atomic scattering factors and the anomalous dispersion coefficients were from International Tables for X-Ray Crystallography[6].

TABLE I

Experimental Data for the Crystallographic Analyses

Compound	etu	AgCl · 2etu	AgBr · 2etu
Formula	$C_3H_6N_2S$	$AgCl(C_3H_6N_2S)_2$	$AgBr(C_3H_6N_2S)_2$
F. W.	102.15	347.6	392.1
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/n$
$a/\text{Å}$	5.801(3)	11.078(4)	9.050(1)
$b/\text{Å}$	14.540(5)	14.046(6)	10.557(3)
$c/\text{Å}$	5.774(3)	7.749(2)	13.191(4)
$\beta/°$	101.3(1)	103.71(2)	103.38(1)
$V/\text{Å}^3$	477.6(4)	1171.4(7)	1226.1(5)
Z	4	4	4
$D_m/\text{Mg m}^{-3}$ (flotation)	1.45	1.96	2.00
$D_c/\text{Mg m}^{-3}$	1.421	1.971	2.124
reflections for ⎧number	—	22	22
lattice parameters ⎩Θ-range	—	7°—21.5°	9°—24°
crystal data radiation	—	Mo—Kα_1	Mo—Kα_1
wavelength/Å	—	0.709300	0.709300
F(000)	216	688	760
temperature/K	293(1)	293(1)	293(1)
crystal size/mm³	0.16×0.24×0.33	0.11×0.18×0.26	0.27×0.39×0.27
diffractometer	SIEMENS-AED	Philips PW1100	Philips PW1100
μ/mm^{-1}	0.490	2.247	5.156
absorption correction (min-max)	—	0.732—1.258	0.823—1.211
extinction correction (min-max)	—	0.863—1.008	0.909—1.019
Θ-range	3°—23°	3°—30°	3°—30°
h-range	$\overline{6}$—6	0—16	$\overline{13}$—13
k-range	$\overline{15}$—15	0—20	0—15
l-range	0—6	$\overline{11}$—11	0—18
standard reflection	$\overline{1}$ 4 1	3 2 1	1 $\overline{1}$ 4
intensity variation	none	none	none
scan speed/degr s^{-1}	0.01—0.04	0.05	0.05
scan width/°	1.20+0.33 tanΘ	0.60+0.20 tanΘ	0.60+0.20 tanΘ
no. of measured reflections	1461	3702	3875
condition for observed reflections	I > 3σ (I)	I > 3σ (I)	I > 3σ (I)
no. of unique reflections	506	1372	1976
method for solving the structure	—	Patterson-Fourier	Patterson-Fourier
anisotropic least-squares on F	full matrix	full matrix	full matrix
max. least-squares shift to error ratio	0.014	0.24	0.25
max./min. height in final difference synthesis	0.069/—0.060	0.28/—0.33	0.18/—0.34
no. of refined parameters	109	175	175
$R =$	0.0235	0.0558	0.0379
$R_w =$	0.0284	0.0619	0.0442
$S =$	0.6873	1.7278	1.3166
k, g ($w = k/[\sigma^2 (F_0) + gF_0^2]$)	0.6405, 0.000378	2.5895, 0.000113	1.3484, 0.000323

The final atomic coordinates with the mean-square displacements along the principal axes of the thermal ellipsoids, the equivalent isotropic thermal parameters, B_{eq}[8], and the ratios of the maximum and minimum principal axes of the thermal ellipsoids are quoted in Table II. The results for the two metal-complexes correspond to the refinements with absorption corrected data. Observed and calculated structure factors with anisotropic thermal parameters have been deposited with the Editor.

TABLE II

Fractional Atomic Coordinates, Principal Axes of Thermal Ellipsoids (r_1, r_2, r_3, $\times 10^4$ Å^2), B_{eq}/Å^2 and Ratios r_{max}/r_{min}

Atom	x	y	z	r_1	r_2	r_3	B_{eq}	r_{max}/r_{min}
AgCl · 2etu								
Ag	0.25043(8)	0.17195(7)	0.05211(13)	673(8)	466(8)	333(6)	3.88(3)	2.02
C1	0.1698(3)	−0.0114(2)	−0.0409(4)	733(26)	396(24)	348(21)	3.89(8)	2.11
S1	0.4825(3)	0.1529(2)	0.1366(5)	668(23)	380(15)	324(17)	3.61(8)	2.06
S2	0.1394(3)	0.2133(2)	0.3112(4)	529(22)	386(20)	279(14)	3.14(8)	1.90
N11	0.4248(10)	−0.0143(7)	0.2671(14)	633(72)	469(85)	324(58)	3.75(30)	1.95
N21	0.6210(10)	0.0042(8)	0.2756(15)	806(89)	546(78)	294(64)	4.33(35)	2.74
N12	−0.0096(10)	0.3648(8)	0.1967(13)	810(93)	423(66)	232(57)	3.86(33)	3.50
N22	−0.0809(9)	0.2319(7)	0.0773(14)	713(91)	521(72)	260(61)	3.93(34)	2.74
C11	0.5092(10)	0.0436(8)	0.2262(15)	578(79)	318(62)	300(84)	3.15(32)	1.93
C21	0.4776(14)	−0.1096(9)	0.3205(20)	811(106)	494(98)	288(70)	4.19(43)	2.82
C31	0.6165(13)	−0.0929(10)	0.3428(21)	719(81)	598(126)	276(85)	4.19(42)	2.61
C12	0.0129(10)	0.2723(8)	0.1913(14)	452(71)	350(85)	244(61)	2.75(31)	1.85
C22	−0.1242(14)	0.3929(11)	0.0718(21)	840(124)	540(92)	421(97)	4.74(45)	2.00
C32	−0.1807(12)	0.2987(10)	0.0024(20)	683(102)	560(110)	383(75)	4.28(42)	1.78
H11	0.342(11)	0.0028(8)	0.255(15)	—	—	—	8.2(30)	—
H21	0.675(11)	0.029(8)	0.248(15)	—	—	—	9.9(30)	—
H12	0.037(11)	0.397(8)	0.268(15)	—	—	—	4.3(30)	—
H22	0.082(11)	0.173(9)	0.083(16)	—	—	—	6.7(30)	—
H31	0.454(11)	−0.147(9)	0.240(16)	—	—	—	3.2(29)	—
H41	0.456(11)	−0.131(8)	0.429(16)	—	—	—	2.5(30)	—
H61	0.659(11)	−0.098(8)	0.498(16)	—	—	—	5.6(30)	—
H51	0.663(11)	−0.132(9)	0.266(16)	—	—	—	5.5(30)	—
H32	−0.090(11)	0.443(9)	−0.023(16)	—	—	—	8.2(31)	—
H42	−0.166(11)	0.413(9)	0.123(15)	—	—	—	6.8(30)	—
H62	−0.251(11)	0.293(9)	0.039(15)	—	—	—	6.4(31)	—
H52	−0.202(11)	0.296(8)	−0.121(16)	—	—	—	9.0(31)	—
AgBr · 2etu								
Ag	0.22790(6)	0.01983(5)	0.05650(4)	527(12)	451(18)	348(6)	3.49(1)	1.51
Br	−0.03226(7)	0.16068(6)	0.06768(5)	500(6)	336(15)	285(11)	2.95(2)	1.76
S1	0.3471(2)	−0.0935(2)	0.2198(1)	739(12)	381(11)	310(11)	3.76(5)	2.38
S2	0.3753(2)	0.1326(2)	−0.0534(1)	670(11)	364(14)	298(11)	3.50(5)	2.25

Atom	x	y	z	r_1	r_2	r_3	B_{eq}	r_{max}/r_{min}
N21	0.3288(7)	−0.0665(6)	0.4185(4)	921(47)	378(46)	324(34)	4.27(18)	2.84
N11	0.1809(7)	0.0618(6)	0.3137(4)	912(40)	392(43)	212(34)	3.99(17)	4.30
N22	0.2803(7)	0.2405(7)	−0.24075	1175(51)	394(32)	311(53)	4.95(22)	3.78
N12	0.0976(6)	0.2048(6)	−0.1660(4)	874(39)	364(33)	288(44)	4.02(19)	3.03
C11	0.2829(7)	−0.0300(5)	0.3202(5)	434(48)	396(42)	282(33)	2.93(15)	1.54
C31	0.2488(10)	−0.0031(7)	0.4866(6)	844(47)	438(52)	403(61)	4.43(25)	2.09
C21	0.1585(10)	0.0962(8)	0.4157(6)	951(50)	467(62)	343(60)	4.63(25)	2.77
C12	0.2444(6)	0.1929(5)	−0.1558(5)	412(39)	372(35)	215(37)	2.63(15)	1.92
C32	0.1462(9)	0.2865(10)	−0.3168(7)	1134(70)	485(48)	401(67)	5.32(27)	2.83
C22	0.0227(8)	0.2633(10)	−0.2619(7)	1094(67)	573(69)	322(42)	5.23(26)	3.40
H21	0.370(8)	−0.128(7)	0.433(5)	—	—	—	10.9(17)	—
H11	0.148(8)	0.104(7)	0.265(5)	—	—	—	5.8(17)	—
H22	0.388(8)	0.234(7)	−0.248(5)	—	—	—	5.1(17)	—
H12	0.0468(8)	0.178(6)	−0.125(6)	—	—	—	7.4(17)	—
H61	0.3278(8)	0.044(6)	0.546(6)	—	—	—	8.4(17)	—
H51	0.1828(8)	−0.064(7)	0.505(5)	—	—	—	7.0(17)	—
H31	0.0398(8)	0.096(7)	0.405(5)	—	—	—	8.3(17)	—
H41	0.1848(8)	0.181(7)	0.427(6)	—	—	—	6.5(17)	—
H62	0.138(8)	0.239(7)	−0.381(6)	—	—	—	6.4(17)	—
H52	0.173(8)	0.378(7)	−0.319(5)	—	—	—	8.6(18)	—
H32	−0.0418(8)	0.331(7)	−0.250(6)	—	—	—	8.9(17)	—
H42	−0.050(8)	0.218(7)	−0.301(6)	—	—	—	7.1(17)	—
etu								
S	0.22603(11)	0.61408(5)	0.04402(12)	516(30)	471(35)	290(6)	3.36(2)	1.78
N2	0.47157(42)	0.67651(17)	0.45723(45)	637(20)	346(15)	269(17)	3.30(7)	2.37
N1	0.64730(50)	0.56776(20)	0.30619(49)	822(19)	382(16)	261(19)	3.85(8)	3.15
C1	0.45464(39)	0.61934(15)	0.27493(40)	382(16)	317(21)	255(19)	2.51(7)	1.50
C3	0.69043(56)	0.66697(23)	0.62830(59)	571(24)	410(17)	274(20)	3.30(9)	2.08
C2	0.81572(60)	0.59067(23)	0.51937(59)	534(24)	394(29)	330(20)	3.31(9)	1.62
H2	0.3720(42)	0.7207(19)	0.4623(43)	—	—	—	3.7(9)	—
H5	0.7683(41)	0.7233(20)	0.6400(46)	—	—	—	3.6(9)	—
H6	0.6479(58)	0.6493(20)	0.7893(46)	—	—	—	6.4(13)	—
H4	0.8533(55)	0.5364(21)	0.6333(51)	—	—	—	5.8(13)	—
H3	0.9638(48)	0.6117(20)	0.4802(45)	—	—	—	4.3(9)	—
H1	0.6709(50)	0.5260(20)	0.2061(46)	—	—	—	4.2(11)	—

The calculations were carried out on the CYBER 76 computer of the *Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord--Orientale* (CINECA, Casalecchio, Bologna), with the financial support of the University of Parma, and the GOULD-SEL 32/77 computer of the »Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)«. In addition to the quoted SHELX program, LQPARM[9], ASSORB[10], PARST[11], XANADU[12], ORTEP[13] programs have been used.

Through all the paper an average value, $\langle x \rangle$, is a weighted mean and the corresponding e.s.d., σ, is the larger of the values of σ_e and σ_i [14] given by the formulae:

$$\langle x \rangle = \Sigma_s\, w_s\, x_s / \Sigma_s\, w_s$$

$$\sigma_e = \left\{ \left(\frac{\Sigma_s\, w_s\, x_s^2}{\Sigma_s\, w_s} - \langle x \rangle^2 \right) / (N-1) \right\}^{1/2}$$

$$\sigma_i = (\Sigma_s\, w_s)^{-1/2}$$

$$w_s = 1/\sigma_s^2$$

When two values, x_1 and x_2, are compared, the ratio $\Delta/\sigma = |x_1 - x_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ is considered, where σ_1 and σ_2 are the e.s.d.'s of x_1 and x_2 respectively.

3. DISCUSSION

3.1. *Thermal Motion*

The three structure analyses are accurate enough (particularly that of uncomplexed ethylene thiourea) to allow some discussion of thermal motion and to allow the use of thermal parameters to analyze the motion of the etu molecules in terms of rigid body libration.

From the B_{eq}'s and the root mean square displacements along the principal axes of the thermal ellipsoids quoted in Table 2 and from Figure 1 and 2, it
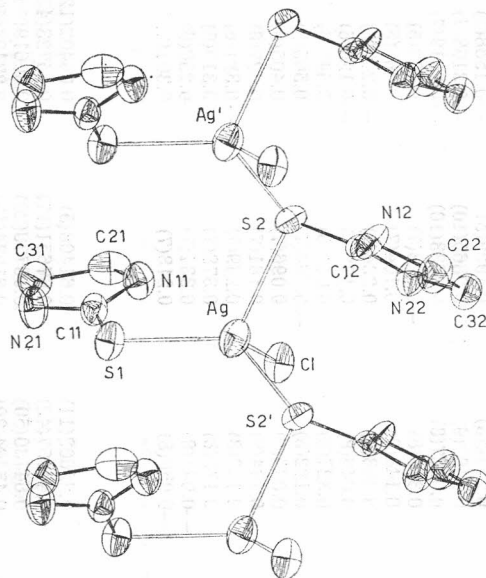

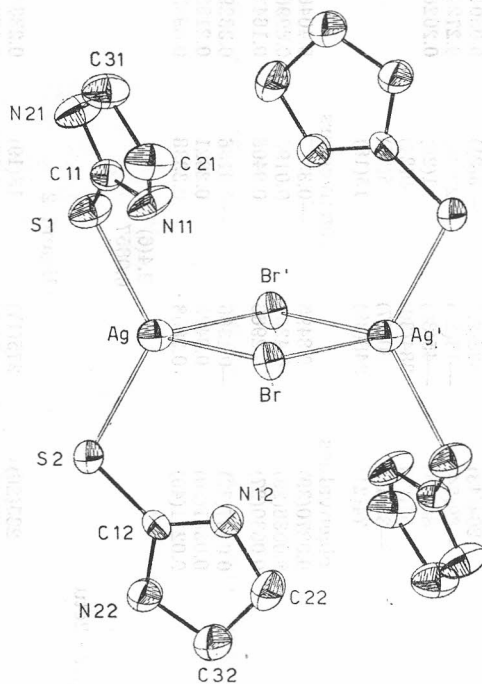Figure 1. Chains of coordination polyhedra in AgCl · 2etu. Thermal ellipsoids at 50⁰/₀ probability (ORTEP).

Figure 2. Dimers in AgBr · 2etu. Thermal ellipsoids at 50% probability (ORTEP).

can be inferred that the thermal motion of the silver and halogen atoms is a little higher in the chlorine than in the bromine derivative, and this may be related not only to the difference of the mass of the halogen atoms, but also to the bonds the silver atom forms with them and sulphur. In fact, the two Ag—Br distances, 2.817(1) and 2.847(1) Å, are only 0.052(3) and 0.082(3) Å longer than the Ag—Cl = 2.765(3) Å distance, and these differences are both relatively shorter than the difference, 0.15 Å, between the covalent (or ionic) radii of the two halogen atoms. Moreover, the two Ag—S distances in the bromine complex, 2.482(2) and 2.489(2) Å, are both shorter than all the Ag—S distances in the chlorine complex [2.512(3), 2.551(3), 2.655(4) Å].

Concerning the anisotropy of motion, it can be observed that, while the anisotropy is a little higher for Ag and Cl in the chlorine derivative, if compared with Ag and Br in the bromine derivative, the sulphur atoms show a little larger anisotropy in the bromine than in the chlorine derivative.

Comparing the thermal motion of the etu ligands in the two complexes with that in uncomplexed etu (Table III), it is seen that the average motion (not considering hydrogens) shows a small increase from etu ($B_{av.}$ = 3.3(1) Å^2) to AgCl · 2etu ($B_{av.}$ = 3.5(1) Å^2) and to AgBr · 2etu ($B_{av.}$ = 3.7(1) Å^2). The results of the rigid body libration analysis[15], quoted in Table III, show that the model is quite satisfactory particularly for uncomplexed etu, confirming also the general accuracy of these structural determinations and the reliability of the corrections of bond distances deduced by the analysis. In Table III are also quoted the results of the analysis of the rigid body librational motion of

TABLE III

Librational Tensors for etu: $L_{ij}/(rad^2 \times 10^{-4})$, $T_{ij}/(Å^2 \times 10^{-4})$, $S_{ij}/(rad \times Å \times 10^{-4})$, $\varrho_i/Å$, $R(U) = \Sigma|\Delta U_{ij}|/\Sigma|U_{ij}|$ Referred to an Orthogonal System of Axes Such That Z Lies Along z, Y is in the Plane of y and z, and X Completes a Right-Handed set. ϱ_i's are the Origin Shifts Required to Symmetrize S. LLA = Largest Libration Amplitude

ij	L_{ij}	T_{ij}	S_{ij}	ϱ_i	L_{ij}	T_{ij}	S_{ij}	ϱ_i
	ligand 1				ligand 2			
AgCl · 2etu								
11	38(20)	317(34)	−16(18)	0.5003	204(43)	368(25)	−6(21)	0.0504
12	−39(25)	33(28)	−1(17)	0.0274	−69(24)	−13(22)	22(36)	0.2724
13	14(16)	−36(36)	34(12)	0.2274	80(26)	−45(30)	1(26)	0.2026
22	247(66)	335(30)	20(26)		57(26)	384(30)	−9(24)	
23	−89(36)	−34(35)	4(30)		−33(16)	−60(27)	5(25)	
33	87(27)	388(58)	−4(18)		74(21)	248(39)	15(18)	
	eigenvalues		eigenvectors		eigenvalues		eigenvectors	
L_1	0.0293(62)	0.1598	−0.9025	0.4001	0.0270(39)	0.8495	−0.3385	0.4046
L_2	0.0048(32)	−0.1784	0.3722	0.9109	0.0036(29)	−0.4362	−0.0195	0.8996
L_3	0.0031(22)	0.9709	0.2169	0.1015	0.0030(27)	0.2966	0.9408	0.1643
T_1	0.0425(51)	−0.4022	−0.4480	0.7984	0.0407(32)	−0.1366	−0.9136	0.3829
T_2	0.0324(45)	0.3667	0.7202	0.5889	0.0381(30)	−0.9485	0.2321	0.2155
T_3	0.0291(36)	0.8389	−0.5297	0.1254	0.0211(40)	0.2858	0.3338	0.8983
LLA	9.8(10)°				9.4(6)°			
R(U)	0.1107				0.0857			
	ligand 1				ligand 2			
AgBr · 2etu								
11	74(16)	353(30)	20(11)	0.2735	235(26)	275(17)	13(19)	0.2384
12	−57(14)	26(28)	4(9)	−0.0153	−95(16)	−33(17)	−1(18)	0.1798
13	−107(19)	19(18)	−3(11)	0.3365	175(16)	33(15)	−3(17)	−0.1429
22	99(17)	269(28)	−12(12)		111(16)	326(29)	−11(12)	
23	111(19)	36(17)	21(12)		−145(16)	18(21)	6(9)	
33	383(42)	367(17)	−8(16)		296(24)	331(20)	−2(16)	
	eigenvalues		eigenvectors		eigenvalues		eigenvectors	
L_1	0.0459(36)	−0.2979	0.3244	0.8978	0.0516(25)	0.5776	−0.3916	0.7163
L_2	0.0071(22)	0.4489	−0.7824	0.4316	0.0094(25)	−0.8162	−0.2871	0.5013
L_3	0.0027(19)	0.8425	0.5316	0.0874	0.0032(18)	−0.0093	0.8742	0.4854

AgSCN · 2etu

ij	L_{ij}	T_{ij}	S_{ij}	ϱ_i	L_{ij}	T_{ij}	S_{ij}	ϱ_i
T_1	0.0396(24)	0.5434	0.3305	0.7717	0.0347(23)	0.2161	0.4113	0.8855
T_2	0.0340(27)	—0.8164	—0.0062	0.5775	0.0342(24)	0.5253	—0.8135	0.2497
T_3	0.0253(27)	0.1956	—0.9438	0.2665	0.0243(22)	—0.8230	—0.4112	0.3919
LLA		12.3(5)°				13.0(3)°		
R(U)		0.0659				0.0498		
		ligand 1				ligand 2		
11	26(6)	216(13)	—5(6)	0.6891	141(15)	249(11)	3(5)	0.1491
12	—20(5)	12(12)	7(5)	0.0212	—85(10)	3(11)	7(5)	0.6224
13	—8(9)	1(10)	2(5)	0.1140	—12(7)	5(8)	5(7)	0.6039
22	63(8)	167(14)	1(6)		71(11)	155(12)	—18(5)	
23	—74(10)	—5(9)	—3(5)		7(5)	—9(9)	1(6)	
33	223(21)	200(9)	4(8)		36(6)	184(9)	15(5)	
	eigenvalues	eigenvectors			eigenvalues	eigenvectors		
L_1	0.0252(20)	—0.0007	—0.3646	0.9312	0.0199(14)	—0.8281	0.5541	0.0847
L_2	0.0052(8)	—0.6391	0.7164	0.2800	0.0035(6)	0.0474	—0.0814	0.9956
L_3	0.0008(8)	0.7691	0.5949	0.2335	0.0014(13)	0.5585	0.8285	0.0412
S_1	0.0219(14)	—0.9740	—0.2265	0.0085	0.0249(11)	0.9970	0.0247	0.0728
S_2	0.0201(9)	0.0395	—0.1328	0.9904	0.0186(9)	—0.0629	—0.2812	0.9576
S_3	0.0164(14)	—0.2232	0.9649	0.1383	0.0152(12)	—0.0442	0.9593	0.2789
LLA		9.1(4)°				8.1(3)°		
R(U)		0.0515				0.0509		
		etu						
11	278(18)	309(10)	—5(6)	0.5484				
12	—5(7)	—29(11)	4(6)	0.6269				
13	179(12)	23(10)	5(7)	0.3885				
22	35(5)	268(14)	—1(5)					
23	—4(7)	12(13)	7(4)					
33	161(14)	253(12)	6(6)					
	eigenvalues	eigenvectors						
L_1	0.0408(17)	0.8094	—0.0172	0.5870				
L_2	0.0035(5)	—0.0613	—0.9966	0.0554				
L_3	0.0031(15)	—0.5841	0.0808	0.8077				
S_1	0.0327(12)	0.8940	—0.3942	0.2131				
S_2	0.0272(16)	0.1666	0.7338	0.6586				
S_3	0.0231(15)	—0.4161	—0.5533	0.7217				
LLA		11.6(2)°						
R(U)		0.0402						

etu in AgSCN · 2etu after further refinement ($R = 0.0410$) of the data published by Belicchi Ferrari, Gasparri Fava and Vidoni Tani[16]. From the data quoted in that table and Figure 3 it appears that the etu molecules undergo the same kind of motion in these compounds with the largest librational amplitude ranging from 8° to 13° along the axis of the minimum moment of inertia.
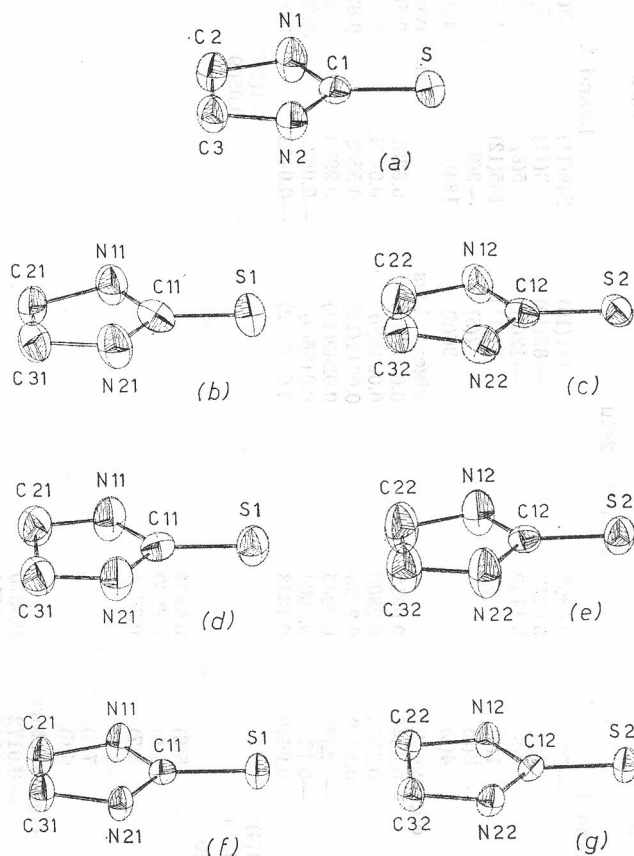

Figure 3. Atomic thermal ellipsoids at 50% probability (ORTEP) of: (a) etu, (b) and (c) AgCl · 2etu, (d) and (e) AgBr · 2etu, (f) and (g) AgSCN · 2etu.

## 3.2. *Description of the Structures of the Complexes*

As shown in Figure 1 and 2, silver coordination is distorted tetrahedral in both compounds with bridging ligand atoms, but, in the case of the chlorine derivative, the structure is polymeric and bridging involves the sulphur atom of an etu ligand, while in the bromine complex it is the halogen atom that bridges two silver atoms giving rise to a centrosymmetric dimeric compound. The deformations of the coordination tetrahedra can be inferred from the data quoted in Table IV and more clearly from the projections of Figure 4 which shows also the orientation of the S—C bonds with respect to the coordination polyhedra.

TABLE IV

*Bond Distances and Angles of the Metal Environments*

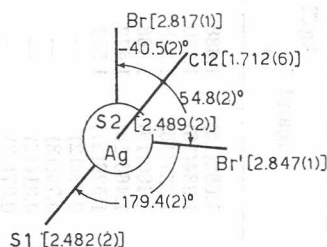| AgCl · 2etu		AgBr · 2etu	
Ag—Cl	2.765(3) Å	Ag—Br	2.817(1) Å
Ag—S1	2.512(3)	Ag—Br'	2.847(1)
Ag—S2	2.655(4)	Ag—S1	2.482(2)
Ag—S2'	2.551(3)	Ag—S2	2.489(2)
Ag . . . Ag'	4.452(2)	Ag . . . Ag'	4.070(1)
Cl—Ag—S1	102.5(1)°	Br—Ag—Br'	88.13(3)°
Cl—Ag—S2	102.8(1)	Br—Ag—S1	114.19(6)
Cl—Ag—S2'	109.1(1)	Br—Ag—S2	110.19(5)
S1—Ag—S2	117.1(1)	S1—Ag—S2	123.53(7)
S1—Ag—S2'	123.0(1)	S1—Ag—Br'	105.31(5)
S2—Ag—S2'	100.7(1)	S2—Ag—Br'	109.32(6)
Ag—S1—C11	105.9(4)	Ag—S1—C11	109.1(2)
Ag'—S2—C12	106.5(4)	Ag—S2—C12	105.8(2)
Ag—S1—C11—N21	174.8(10)	Ag—S1—C11—N21	—177.6(5)
Ag'—S2—C12—N22	—166.2(9)	Ag—S2—C12—N22	—167.9(5)

(Ag—S—C) av. = 107.8(9)°
(Ag—S—C—N) av. = 172.2(3)°
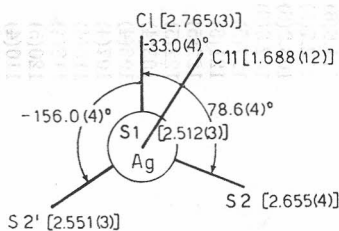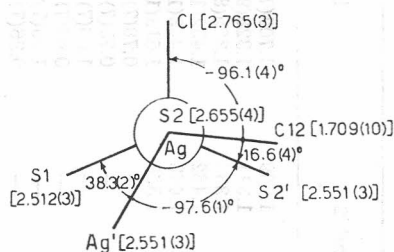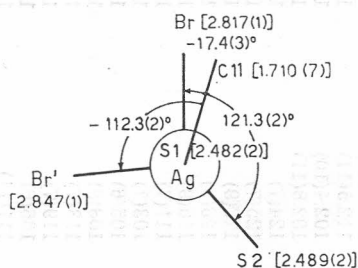
Figure 4. Newman projections showing the reciprocal orientation of the ligands about the metal centres: (a) along S1—Ag, (b) along S2—Ag in AgCl · 2etu; (c) along S1—Ag, (d) along S2—Ag in AgBr · 2etu. The values in square brackets are the distances of the atoms from silver or sulphur.

TABLE V

Bond Distances (Å) and Angles (deg) in Ethylenethiourea.* Values Corrected for Librational Motion.

	AgCl · 2etu ligand 1	*	AgCl · 2etu ligand 2	*	AgBr · 2etu ligand 1	*	AgBr · 2etu ligand 2	*	etu	*
S—C1	1.682(12)	1.688	1.703(10)	1.709	1.702(7)	1.710	1.701(6)	1.712	1.688(3)	1.694
C1—N1	1.334(16)	1.350	1.324(15)	1.341	1.328(9)	1.253	1.310(8)	1.338	1.329(4)	1.353
C1—N2	1.327(15)	1.345	1.321(14)	1.334	1.325(8)	1.347	1.335(9)	1.359	1.330(3)	1.347
N1—C2	1.480(16)	1.488	1.457(17)	1.462	1.452(11)	1.460	1.430(10)	1.440	1.452(4)	1.460
N2—C3	1.465(18)	1.472	1.461(16)	1.468	1.443(11)	1.452	1.467(10)	1.479	1.454(4)	1.460
C2—C3	1.526(21)	1.552	1.507(20)	1.529	1.513(11)	1.550	1.487(13)	1.527	1.528(5)	1.561
N1—H1	0.93(12)	—	0.80(11)	—	0.78(7)	—	0.85(8)	—	0.87(3)	—
N2—H2	0.76(13)	—	0.83(12)	—	0.75(7)	—	1.00(8)	—	0.87(3)	—
C2—H3	0.81(12)	—	1.15(13)	—	1.06(7)	—	0.95(7)	—	0.98(3)	—
C2—H4	0.97(13)	—	0.74(14)	—	0.92(7)	—	0.87(7)	—	1.02(3)	—
C3—H6	1.19(12)	—	0.90(13)	—	1.05(7)	—	0.97(8)	—	1.04(3)	—
C3—H5	1.03(13)	—	0.93(12)	—	0.96(7)	—	1.00(8)	—	0.93(3)	—
S—C1—N1	126.1(9)		126.6(9)		126.5(5)		128.4(5)		126.3(2)	
S—C1—N2	124.1(9)		124.8(9)		124.1(5)		123.2(5)		125.3(2)	
N1—C1—N2	109.7(10)		108.6(10)		109.3(6)		108.4(6)		108.4(2)	
C1—N1—C2	111.4(11)		112.7(11)		111.6(6)		113.2(6)		113.3(2)	
C1—N2—C3	112.5(11)		113.0(10)		112.7(6)		112.1(6)		113.4(3)	
N1—C2—C3	102.4(10)		102.8(12)		103.2(6)		104.2(7)		102.7(3)	
N2—C3—C2	102.8(11)		102.1(11)		102.3(6)		102.0(7)		102.2(3)	
C1—N1—H1	124(7)		119(8)		127(5)		127(5)		123(2)	
C2—N1—H1	125(7)		129(8)		121(5)		120(5)		124(2)	
C1—N2—H2	118(9)		115(8)		122(5)		119(4)		123(2)	
C3—N2—H2	128(9)		130(9)		122(5)		128(4)		123(2)	
N1—C2—H3	110(9)		103(6)		103(4)		111(4)		111(2)	
N1—C2—H4	111(7)		108(9)		108(4)		115(4)		113(2)	
N2—C3—H5	103(7)		111(7)		107(4)		100(4)		108(2)	
N2—C3—H6	105(6)		117(8)		110(4)		108(4)		108(2)	
C3—C2—H3	108(9)		119(6)		118(4)		121(4)		112(2)	
C3—C2—H4	113(7)		106(10)		120(5)		111(5)		111(2)	
C2—C3—H5	119(7)		113(7)		110(4)		113(4)		114(2)	
C2—C3—H6	105(6)		107(8)		108(4)		115(4)		114(2)	
H3—C2—H4	111(11)		117(11)		104(6)		96(7)		108(2)	
H5—C3—H6	115(9)		107(11)		119(6)		117(6)		110(2)	

Even if a rigorous discussion of the nature of the bonds in terms of MO theory could be attempted only on the basis of observed, and calculated deformed electron density distributions, nevertheless, something could be deduced from the geometrical situation of the etu ligands in these complexes. Indeed, the values of the torsion angles Ag—S—C—N [172.2(3)° av.] indicate that in both complexes the metal atom shows a tendency to be coplanar with the etu molecule, and the bond angles Ag—S—C [107.8(9)° av.] strongly suggest that the bond is due to an interaction involving a sulphur (sp²?) lone pair and a suitable sp³ silver orbital. The bridging character of S2 in the chlorine derivative could be explained by an additional d—π interaction involving a metal d-orbital and a ligand π-orbital, as indicated by the angle Ag—S2——C12 = 99.4(4)°.

From the data of Tables V and VI it appears that, if exception is made for the S—C—N angles, no significant variations are observed for the geometry of the etu molecules, acting as terminal or bridging ligands, compared with uncoordinated etu. Comparison, of course, must be made on data corrected for librational motion and the averaging for the values quoted in Table VI appears justified. The two angles S—C—N and S—C—N' are significantly different (Δ/σ = 3.54) in uncomplexed etu and this deformation may be due to the asymmetry of the contacts the N—H groups form with sulphur atoms of adjacent molecules. The difference between these two S—C—N angles is systematic and much larger in the case of the complexes: the S—C—N angle on the side of the lone pair interacting with metal is always significantly larger than the S—C—N' angle on the other side, and this seems to be a peculiar character of the etu metal complexes (Table VII).

TABLE VI

Comparison of Averaged Bond Distances and Angles in Ethylenethiourea. Bond Distances are Corrected for the Rigid Body Librational Motion

	Ag complexes (*)	uncomplexed etu	Δ/σ
S — C(sp²)	1.699(4)Å	1.694(3)Å	1.00
N — C(sp²)	1.342(2)	1.349(3)	1.94
N — C(sp³)	1.459(3)	1.460(3)	0.24
C(sp³) — C(sp³)	1.531(6)	1.561(5)	3.84
S — C(sp²) — N	126.6(3)	126.3(2)	0.83
S — C(sp²) — N'	124.3(2)	125.3(2)	3.54
N — C(sp²) — N'	109.1(2)	108.4(2)	2.48
C(sp²) — N — C(sp³)	112.3(1)	113.3(2)	4.47
N — C(sp³) — C(sp³)	102.8(1)	102.5(3)	0.95
Σ₁	360.0(4)	360.0(3)	
Σ₂	539.3(3)	540.0(5)	

Σ₁ sum of the angles around C(sp²)
Σ₂ sum of the endocyclic angles

(*) In the averages the values from AgSCN · 2etu are also considered.

TABLE VII

Comparison of the Angles About the C (sp²) Carbon Atom in etu-Complexes

Compound	R	S—C—N	S—C—N′	N—C—N′	References
AgCl · 2etu	0.056	126.1(9)°	124.1(9)°	109.7(10)°	present study
		126.6(9)	124.8(9)	108.6(10)	
AgBr · 2etu	0.038	126.5(5)	124.1(5)	109.3(6)	present study
		128.4(5)	123.2(5)	108.4(6)	
AgSCN · 2etu#	0.041	126.5(3)	124.9(3)	108.6(3)	(16)
		126.2(3)	124.1(3)	109.7(3)	
Te(ClO₄)₂ · 3etu	0.053	130.0(8)	125.7(8)	104.3(9)	(17)
		128.5(8)	120.3(8)	110.9(9)	
		129.0(7)	121.1(7)	109.9(8)	
Te₂Cl₄ · 4etu	0.056	127.2(9)	121.9(9)	110.9(10)	(18)
		127.5(9)	120.8(8)	111.6(10)	
TeCl₂ · 4etu · 2H₂O*	0.039	124.8(8)	124.8(9)	110.5(10)	(19)
		125.5(8)	123.9(9)	110.6(10)	
		128.1(8)	122.6(9)	109.3(10)	
		128.8(9)	121.9(10)	109.3(10)	
TeBr₂ · 4etu orthorhombic	0.043	126.4(8)	120.6(7)	113.0(9)	(20)
TeBr₂ · 4etu monoclinic	0.032	126.6(5)	122.0(5)	111.4(6)	(20)
		128.0(4)	120.4(4)	111.6(5)	
AuCl · 2etu · H₂O	0.084	126.9(17)	121.9(14)	111.1(18)	(21)
		127.4(19)	122.0(16)	110.5(19)	
C₆H₅TeCl · etu	0.024	125.5(2)	123.2(2)	111.3(2)	(22)
C₆H₅TeBr · etu yellow	0.028	127.6(3)	122.1(3)	110.3(3)	(23)
C₆H₅TeBr · etu orange red	0.033	126.1(3)	123.4(3)	110.4(4)	(23)
C₆H₅TeI · etu	0.037	128.1(4)	120.6(4)	111.3(5)	(24)
Te(CH₃S₂O₂)₂ · 2etu triclinic	0.091	124.0(13)	121.5(17)	114.5(18)	(25)
Te(CH₃S₂O₂)₂ · 2etu monoclinic	0.068	125.6(15)	124.9(16)	109.5(16)	(25)
Te(C₆H₅S₂O₂)₂ · 2etu	0.081	124.9(13)	122.1(10)	113.0(14)	(26)
Te(SCN)₂ · 2etu*	0.070	126.9(⁺)	123.1(⁺)	110.0(⁺)	(27)
Te(SeCN)₂ · 2etu*	0.065	124.5(⁺)	123.8(⁺)	111.5(⁺)	(27)
Co(CH₃COO)₂ · 2etu	0.061	129.3(8)	125.3(8)	105.4(9)	(28)
NiCl₂ · 4etu triclinic	0.066	124.1(13)	124.8(14)	111.1(16)	(29)
		126.1(13)	124.4(14)	109.3(15)	
NiCl₂ · 4etu* monoclinic	0.088	128.7(16)	122.1(19)	107.9(19)	(29)
		122.6(21)	124.4(21)	112.9(23)	
Ni(NCS)₂ · 2etu	0.116	126.1(14)	123.4(15)	110.4(17)	(30)
Cu(NO₃)₂ · 4etu	0.085	126.7(6)	122.7(6)	110.7(6)	(31)
		126.9(6)	123.2(6)	109.8(7)	
		125.6(7)	125.0(6)	109.3(6)	
		124.7(8)	124.7(8)	110.6(7)	
Cu₂Cl₂ · 4etu	0.094	128.6(9)	122.6(8)	108.8(9)	(31)
		123.7(9)	123.0(10)	113.3(11)	
		125.7(9)	124.1(8)	110.2(9)	
		125.7(10)	124.1(9)	110.2(9)	
BiCl₃ · 2etu	0.049	127.0(10)	120.0(10)	112.0(10)	(32)
av.		126.7(2)	123.1(2)	110.3(2)	

* Values calculated from published atomic coordinates.

(⁺) The e.s.d.'s of the atomic coordinates are missing in the original paper, so these data are not considered in the averages.

After further refinement.

The mutual orientation of the two independent etu ligands in both complexes is quite similar (Figure 1), as indicated also by the dihedral angles their mean planes form: 46.5(4)° and 45.6(2)° for the chlorine and bromine derivative respectively.

3.3. *The Structure of the etu Molecule*

While thiourea has been the subject of several structural investigations[33-41], only one crystal structure analysis has been published on ethylenethiourea[2]. This analysis, based on visually estimated photographic data and on the use of Booth's differential synthesis[42] for isotropic refinement, is a classical example of the best that could be obtained from very accurate work at that time. The necessity for data of higher accuracy, such as those obtainable by more modern experimental and computing techniques, to compare the structure of the uncomplexed molecule with that of the complexed one, prompted us to collect a new set of diffractometer data and to refine the structure by anisotropic least-squares. The experimental conditions are summarized in Table I and the results of the conventional free-atom model all-data refinement are given in Tables II, III and V together with those of the described complexes. As already observed, coordination to metal does not seem to influence in a detectable way the geometry of the ligands, if exception is made for the S—C—N angles.

It is interesting to compare the thiourea moiety of the molecule with thiourea itself. Assuming the results of the free-atom model high angle refinement for thiourea at 123 K,[41] the distances (corrected for rigid body librational motion) and the angle quoted in Table VIII are obtained, which show that, going from tu to etu, the N—C—N angle becomes relevantly narrower [$\Delta = 9.4(2)°$] as a consequence of ring formation. This brings about a decrease in the π-delocalization in the SCN_2 system, consequently the double bond character increases in the S—C bond and decreases in each C—N bond. A valence bond description, based on the use of Pauling's formula[43] relating bond distance to bond order and the values: S—C 1.81, S=C 1.59, N—C 1.48, N=C 1.275 Å, gives the percentages of double bond character (DB%) quoted in Table VIII.

TABLE VIII

Comparison of Bond Distances, d, VB Percentages of Double Bond Character, DB%, and Angles for Uncomplexed tu and etu

	tu*		etu		
	d	DB%	d	DB%	Δ/σ
S—C	1.724(1)Å	17.4	1.694(3)Å	27.0	9.5
calc.	1.725		1.694		
N—C	1.342(1)	41.3	1.349(3)	36.5	2.2
calc.	1.341		1.350		
N—C—N	117.8(1)°	—	108.4(2)°	—	42.0

(*) Averages of two independent molecules.

Another relevant aspect concerning the structure of etu is its lack of planarity which is confirmed by the present analysis. From the data quoted in Table IX, it appears that, considering only the non-hydrogen atoms, the thiourea part of the molecule is strictly planar and the two methylene carbon atoms are significantly displaced from this plane. The hypothesis that the

TABLE IX

Perpendicular Displacements of the Atoms from the Mean SCNN Planes and Total Puckering Amplitudes[44], Q, of the Rings in Complexed and Uncomplexed etu

	AgCl · 2etu		AgBr · 2etu		AgSCN · 2etu		etu
	ligand 1	ligand 2	ligand 1	ligand 2	ligand 1	ligand 2	
S	—0.001(3) Å	0.000(3) Å	0.000(2) Å	0.000(2) Å	0.000(2) Å	0.000(2) Å	0.000(1) Å
Cl	0.020(11)	0.004(11)	—0.001(6)	0.010(6)	0.002(4)	—0.004(4)	0.000(2)
N1	—0.006(10)	—0.001(11)	0.000(6)	—0.004(6)	—0.001(4)	0.001(4)	0.000(3)
N2	—0.007(11)	—0.001(11)	0.000(7)	—0.005(7)	—0.001(4)	0.000(2)	0.000(3)
C2	0.210(14)	0.059(16)	—0.063(9)	—0.030(10)	—0.074(5)	—0.014(4)	0.042(4)
C3	0.076(15)	—0.087(15)	0.091(9)	0.003(10)	0.062(5)	—0.142(4)	0.025(4)
Ag	0.286(1)	—0.567(1)	—0.102(1)	0.539(1)	—0.388(1)	0.181(1)	—
Q	0.104(13)	0.085(14)	0.090(8)	0.020(9)	0.079(5)	0.080(4)	0.015(3)

distortion is due to a bending of the C—S bond out of the plane of the ring does not seem to be confirmed. Comparing the puckering of the different etu rings in complexes, no regular trends can be deduced, suggesting that these distortions are probably due to crystal forces arising from the asymmetry of the surroundings.

3.4 *Hydrogen Bonding and Packing Contacts*

All contacts shorter than the sum of the van der Waals radii can be interpreted as due to hydrogen bonding interactions as shown in Table X. All these bonds involve the N—H groups and the halogens in the case of the metal complexes and sulphur in uncomplexed etu.

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TABLE X

Possible Hydrogen Bonding Contacts

AgCl · 2etu

N11—H11 = 0.93(13) Å	N11...Cl = 3.237(10) Å	H11...Cl = 2.62(11) Å	N11—H11...Cl = 124(9)°
N21—H21 = 0.76(13)	N21...Cl^i = 3.269(13)	H21...Cl^i = 2.63(13)	N21—H21...Cl^i = 143(11)
N12—H12 = 0.81(11)	N12...Cl^{ii} = 3.227(10)	H12...Cl^{ii} = 2.43(11)	N12—H12...Cl^{ii} = 173(11)
N22—H22 = 0.83(12)	N22...Cl^{iii} = 3.242(11)	H22...Cl^{iii} = 2.46(12)	N22—H22...Cl^{iii} = 158(11)

AgBr · 2etu

N21—H21 = 0.75(7) Å	N21...Br^{iv} = 3.400(7) Å	H21...Br^{iv} = 2.67(7) Å	N21—H21...Br^{iv} = 164(7)°
N11—H11 = 0.78(7)	N11...Br = 3.528(5)	H11...Br = 2.80(6)	N11—H11...Br = 156(7)
N22—H22 = 1.00(8)	N22...Br^v = 3.513(7)	H22...Br^v = 2.91(7)	N22—H22...Br^v = 120(6)
N12—H12 = 0.85(8)	N12...Br = 3.574(6)	H12...Br = 2.79(8)	N12—H12...Br = 154(7)

etu

N2—H2 = 0.87(3) Å	N2...S^{vi} = 3.440(3) Å	H2...S^{vi} = 2.62(3) Å	N2—H2...S^{vi} = 158(2)°
N1—H1 = 0.87(3)	N1...S^{vii} = 3.493(3)	H1...S^{vii} = 2.63(3)	N1—H1...S^{vii} = 172(2)

Symmetry codes:

$i = 1 - x, \bar{y}, \bar{z}$ $ii = x, 1/2 - y, 1/2 + z$ $iii = \bar{x}, y, \bar{z}$ $iv = 1/2 - x, y - 1/2, 1/2 - z$ $v = 1/2 + x, 1/2 - y, z - 1/2$

$vi = x, 3/2 - y, 1/2 + z$ $vii = 1 - x, 1 - y, z$

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SAŽETAK

Strukturni aspekti 2-tioimidazolidin koordinacije u srebro(I) halidnim kompleksima

L. P. Battaglia, A. Bonamartini Corradi i M. Nardelli

Iz MoKα difraktometarskih podataka određene su kristalne strukture AgCl · 2etu i AgBr · 2etu (etu = tioimidazolidin = etilentiourea = $SC(NHCH_2)_2$) i ponovno je određena struktura samog etu. AgCl · 2etu: $P2_1/c$, $a = 11,078(4)$ $b = 14,046(6)$, $c = 7,749$ (2) Å, $\beta = 103,71(2)°$, $Z = 4$, konačni R_F (1372) = 0,0558. AgBr · 2etu: $P2_1/n$, $a = 9,050(1)$, $b = 10,557(3)$, $c = 13,191(4)$ Å, $\beta = 103,38(1)°$, $Z = 4$, konačni R_F (1976) = 0,0379. Etu: $P2_1/c$, $a = 5,801(3)$, $b = 14,540(5)$, $c = 5.774(3)$ Å, $\beta = 101,3(1)°$, $Z = 4$, konačni R_F (506) = = 0,0235.

Srebro ima iskrivljenu tetraedarsku koordinaciju u oba kompleksa. Struktura AgCl · 2etu jest polimerna, s jednim terminalnim (Ag—S = 2,512(3) Å) etu-ligandom i jednim premošćujućim preko sumpora (Ag—S = 2,551(3), 2,655(4) Å). Struktura AgBr · 2etu sastoji se od centrosimetričnih dimera s dva terminalna etu-liganda (Ag—S = 2,482(2), 2,489(2) Å) i bromom u mostu (Ag—Br = 2,817(1), 2,847(1) Å).

Karakteristični parametri za nekompleksirani etu jesu: S—C (sp²) = 1,694(3), N—C (sp²) = 1,349(3) prosjek, N—C (sp³) = 1,460(3) prosjek, C (sp³)—C (sp³) = 1,561(5) Å (vrijednosti korigirane za termalno gibanje), N—C—N=108,4(2)°, C—N—C=113.3(2)° prosjek, N—C—C = 102,5(3)° prosjek. Čini se da koordiniranje na metal utječe na kuteve S—C—N: onaj na strani slobodnog elektronskog para uvijek je veći (126,6(3)° prosjek), nego onaj na drugoj strani (124,3(2)° prosjek), dok tiouretski dio liganda zadržava svoju planarnost. Termalno titranje etilentiouree u kristalima prilično je slično, bez obzira da li je kompleksirana ili ne.