Table 4. *Bond angles* (°)

	Cu	Mo	W–B
O(2)–N(1)–O(1)	119·6 (3)	119·9 (3)	120·4 (1)
O(2)–N(1)–O(3)	121·1	120·9	120·5
O(1)–N(1)–O(3)	119·3	119·2	119·0
O(4)–C ---N(3)	116·3	116·7	116·6
O(4)–C ---N(2)	122·0	121·7	121·7
N(3)–C ---N(2)	121·7	121·5	121·7
C ---O(4)–H(5)	119 (4)	113 (4)	113·6 (2)
C ---N(3)–H(4)	123	122	119·1
C ---N(3)–H(3)	119	115	120·8
C ---N(2)–H(1)	117	121	123·1
C ---N(2)–H(2)	127	122	119·1
H(1)–N(2)–H(2)	116 (6)	117 (6)	117·8
H(4)–N(3)–H(3)	118	122	120·1

The bond lengths found in urea nitrate are significantly different from the distances found in the urea molecule (Worsham, Levy & Peterson, 1957). The C–O and C–N distances in urea are 1·243(6) and 1·351(7) Å respectively. It is seen that the C–O distance is lengthened and the C–N distance is shortened when the O atom becomes protonated. Another interesting feature is the large difference in the two O–C–N bond angles in the uronium ion. These effects have also been found in thiourea nitrate (Feil & Song Loong, 1968).

The nitrate group has two short and one long N–O distance. The longer one concerns the oxygen atom involved in the strongest hydrogen bond. In thiourea nitrate two long and one short N–O distance have been found. The oxygen atoms in the long bonds are involved in H-bonding, the short distance oxygen atom is not. The effect of appreciable hydrogen bonding seems to be to stretch the N–O distances.

Inspection of the Tables reveals that differences in the final position parameters of the two sets of measurements (Cu and Mo) are not significant. Comparing our results with those of Worsham & Busing shows that in general the difference in the position parameters is not significant. Differences in vibration parameters, however, are considerable. We believe the neutron results to be more reliable as it is well known that the thermal parameters in an X-ray refinement act as a dustbin for all sorts of errors: no correction for absorption, the use of the wrong atom-factors, neglect of bonding electrons *etc.* The importance of these bonding electrons was shown by the final difference-Fourier synthesis where maxima between atoms showed up clearly. In order to study this effect more carefully, we have started a structure determination at low temperatures.

We thank Dr W.R.Busing and Dr J. E. Worsham for sending a preprint of their paper on the structure of uronium nitrate.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). U.S. Atomic Energy Commission Publication ORNL-TM-305.
DAVIES, M. & HOPKINS, L. (1957). *Trans. Faraday Soc.* **53**, 1563.
FEIL, D. & SONG LOONG, W. (1968). *Acta Cryst.* B**24**, 1334.
JANSSEN, M. J. (1961). *Spectrochim. Acta* **17**, 475.
LONSDALE, K. (1940). *Proc. Royal Soc.* A**177**, 272.
WORSHAM, J. E. & BUSING, W. R. (1968). *Acta Cryst.* B**25**, 572.
WORSHAM, J. E., LEVY, H. A. & PETERSON, S. W. (1957). *Acta Cryst.* **10**, 319.

X-ray powder data, infrared spectra and crystal structures of some bis(selenourea)metal(II) thiocyanates.

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M[XC(NH₂)₂] (NCS)₂ with M = Co, Ni, Cd and X = S, Se, form an isostructuralseries. The structure is polymeric and consists of chains of coordination octahedra linked together by sulphur (or selenium) bridges; the NCS groups are terminal and *trans*-coordinated to metal through the nitrogen atoms.

As a general rule, substitution of selenium for sulphur in a family of compounds gives isostructural crystals*. This is seldom observed, however, in passing from oxygen to sulphur compounds and this behaviour is accounted for by the difference of size, S and Se being smaller than O and S, and by the possibility that selenium and sulphur have to expand their valence shell, using d orbitals in bonding. According to this rule isostructurality is observed for the series of compounds of general formula M[XC(NH₂)₂]₂(NCS)₂ with M = Co,Ni,Cd and X = S,Se. Crystal data from a least-squares procedure applied to powder diffractometer spectra (Cu $K\alpha$) are shown in Table 1 in which the interpretation of the spectra is also given.

The structure of these compounds, already determined for bis(thiourea)nickel(II) thiocyanate (Nardelli, Braibanti

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* One case in which this rule is not observed concerns bis(thiourea)CoCl₂ and bis(selenourea)CoCl₂ prepared by Piovesana & Furlani (1968); the first compound is monoclinic (Co[SC(NH₂)₂]₂Cl₂: $a = 8·13(2)$, $b = 11·78(1)$, $c = 10·79(1)$ Å, $\beta = 103·5°(0·1°)$, $Z = 4$, space group: Cc; the crystals are piezoelectric) the second triclinic (Co[SeC(NH₂)₂]₂Cl₂: $a = 6·08(1)$, $b = 7·22(3)$, $c = 13·86(2)$ Å, $\alpha = 100·7°(0·3°)$, $\beta = 90·2°(0·1°)$, $\gamma = 108·4°(0·1°)$, $Z = 2$); their structures are being studied in our laboratory at present.

& Fava, 1957; Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966), consists of chains of coordination octahedra running along [100], the sulphur (or selenium) atoms being in the bridging positions. The metal atom is surrounded by four sulphur (or selenium) atoms from four thiourea (or selenourea) molecules and two nitrogen atoms from two thiocyanate groups in the *trans* position with respect to the plane of the sulphur (or selenium) atoms.

The similarity of the infrared spectra (Table 2) confirms the isostructurality of all these compounds. The increasing of the N–C–N stretching frequency at 1469 cm^{-1} for thiourea (at 1483 cm^{-1} for selenourea) and the decreasing of the $C=S$ (or the $C=Se$) stretching frequency at 740 cm^{-1}

Table 1. *Powder diffraction data of isostructural*

Ni filtered Cu $K\alpha$ radiation

	Cotu_2(NCS)$_2$			Cosu_2(NCS)$_2$			Nitu_2(NCS)$_2$		
	$a=$ 3·80 (6) Å $\alpha=$ 91·8 (8)°			$a=$ 3·86 (1) Å $\alpha=$ 91·5 (1)°			$a=$ 3·77 (3) Å $\alpha=$ 92·6 (7)°		
	$b=$ 7·53 (8) $\beta=$ 99·5 (9)			$b=$ 7·66 (2) $\beta=$ 103·8 (2)			$b=$ 7·53 (1) $\beta=$ 97·9 (9)		
	$c=$ 10·13 (7) $\gamma=$ 103·6 (9)			$c=$ 10·14 (2) $\gamma=$ 105·1 (2)			$c=$ 10·07 (1) $\gamma=$ 103·6 (9)		
	$V=$ 277·4 Å^3			$V=$ 281·8 Å^3			$V=$ 275·1 Å^3		
hkl	d_o (Å)	d_c (Å)	I/I_1	d_o (Å)	d_c (Å)	I/I_1	d_o (Å)	d_c (Å)	I/I_1
001	9·880	9·997	100	9·782	9·867	100	9·858	9·856	100
010	7·296	7·303	24	7·375	7·373	3	7·260	7·309	10
01$\bar1$	6·117	6·111	16	6·246	6·192	1	6·084	6·119	4
011	5·673	5·694	58	5·655	5·656	12	5·673	5·683	5
002	4·966	4·984	16	4·947	4·933	34	4·950	4·971	3
01$\bar2$				4·332	4·291	<1			
012	3·967	3·982	60	3·941	3·933	25	3·967	3·970	4
100									
10$\bar1$									
020	3·652	3·651	14	3·720	3·686	8	3·655	3·655	2
1$\bar1$0							3·601	3·617	1
02$\bar1$	3·528	3·514	12				3·517	3·519	1
021									
003	3·318	3·323	21	3·311	{ 3·351 / 3·289	33	3·308	3·314	4
10$\bar2$	3·217	3·222					3·168	3·168	1
101							3·245	3·250	1
01$\bar3$	3·116	3·113	19	3·143	3·115	1	3·109	3·110	1
1$\bar2$0				3·048	3·050	8			
11$\bar1$	3·013	3·001	40	3·024	3·011	2	2·972	{ 2·979 / 2·972	5
110									
013	2·934	2·943	6	2·918	2·904	5	2·932	2·934	1
022	2·833	2·847	17	2·844	2·828	8	2·846	2·842	1
1$\bar2$1							2·789	2·789	1
11$\bar2$									
102							2·734	{ 2·737 / 2·733	1
111									
1$\bar2\bar2$									
1$\bar1$3									
02$\bar3$							2·550	2·555	<1
1$\bar2$2									
004	2·490	2·492	14	2·485	2·467	20	2·488	2·486	5
03$\bar1$							2·409	{ 2·410 / 2·408	1
11$\bar3$									
01$\bar4$				2·398	2·408	2			
023							2·366	2·366	1
12$\bar1$							2·321	2·324	1
120									
014	2·301	2·307	30	2·288	2·276	12	2·298	2·300	3
10$\bar4$									
103	2·264	{ 2·261 / 2·261	8						
13$\bar1$									
03$\bar2$							2·258	2·258	1
12$\bar2$							2·222	2·221	1
121	2·189	2·175	8				2·180	2·179	1
02$\bar4$									
1$\bar3$2							2·069	2·067	1
12$\bar3$									
122									
005	1·994	1·994	13	1·989	1·973	11	1·989	1·988	3

for thiourea (at 732 cm^{-1} for selenourea) upon coordination are consistent with the presence of sulphur- (or selenium-) -to-metal bonds as observed by Yamaguchi, Penland, Mizushima, Lane, Curran & Quagliano (1958) and by Swaminathan & Irving (1964). The NCS frequencies indicate an isothiocyanate form for that group coordinated to the metal through the nitrogen atom (Chatt & Duncanson, 1956; Mitchell & Williams, 1960; Pecile, Giacometti & Turco, 1960; Lewis, Nyholm & Smith, 1961; Yagupsky, Negrotti & Levitus, 1965; Nardelli, Fava Gasparri, Musatti & Manfredotti, 1966).

The calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico della

thiourea (tu) and selenourea (su) metal thiocyanates

$(\bar{\lambda} = 1 \cdot 5418 \text{ Å})$. Space group $P\bar{1}$.

	Nisu_2(NCS)$_2$			Cdtu_2(NCS)$_2$			Cdsu_2(NCS)$_2$	
$a=$ 3·80 (1) Å $\alpha=$ 93·5 (1)°			$a=$ 4·04 (1) Å $\alpha=$ 90·8 (1)°			$a=$ 3·97 (1) Å $\alpha=$ 90·3 (1)°		
$b=$ 7·70 (1) $\beta=$ 97·1 (1)			$b=$ 7·68 (1) $\beta=$ 99·7 (1)			$b=$ 7·93 (1) $\beta=$ 99·0 (1)		
$c=$ 10·10 (1) $\gamma=$104·6 (1)			$c=$ 10·10 (1) $\gamma=$105·4 (1)			$c=$ 10·09 (1) $\gamma=$104·0 (1)		
$V=$ 282·3 Å^3			$V=$ 297·7 Å^3			$V=$ 301·6 Å^3		
d_o (Å)	d_c (Å)	I/I_1	d_o (Å)	d_c (Å)	I/I_1	d_o (Å)	d_c (Å)	I/I_1
9·913	9·950	100	9·880	9·957	100	9·880	9·921	100
7·418	7·421	5	7·418	7·387	5	7·583	7·641	1
6·241	6·252	2	6·109	6·076	6	6·259	6·240	1
5·680	5·686	24	5·798	5·799	7	5·821	5·883	2
4·966	4·975	26	4·972	4·979	36	4·955	4·961	45
4·332	4·335	1						
3·953	3·956	32	4·033	4·038	9	4·028	4·050	6
3·625	3·637	1	3·857	3·839	1			
			3·824	3·803	1			
3·715	3·711	7				3·800	3·820	1
			3·548	3·519	2			
3·381	3·370	<1	3·437	3·409	1			
3·317	3·317	<1	3·322	{ 3·322 / 3·322 }	24	3·308	{ 3·307 / 3·308 }	49
3·146	3·146	2						
3·018	3·020	1				3·127	3·131	5
2·970	2·974	<1						
2·920	2·923	3	2·972	2·974	2	2·976	2·970	<1
2·852	2·843	5	2·910	2·899	1	2·960	2·941	1
2·878	2·849	2				2·913	2·902	<1
			2·815	2·822	<1	2·877	2·843	<1
2·638	2·642	1						
2·609	2·607	2						
			2·548	2·531	<1	2·597	2·579	<1
2·543	2·525	1						
2·487	2·488	10	2·492	2·489	18	2·487	2·480	24
2·449	2·458	<1						
2·434	2·428	2				2·454	2·476	1
2·359	2·360	1				2·420	2·428	1
2·315	2·314	2						
2·295	2·291	10	2·324	2·325	7	2·315	2·318	3
			2·274	2·271	1			
2·190	2·177	1	2·232	2·229	1	2·248	2·243	1
						2·138	2·141	1
2·105	2·117	<1						
						2·091	2·094	<1
						2·029	2·032	<1
1·990	1·990	6	1·994	1·992	11	1·989	1·984	9

Table 2. Infrared absorption bands (cm^{-1}) of thiourea (tu) and selenourea (su) metal thiocyanates in 2·5–40 μ*

Thiourea	Cotu$_2$(NCS)$_2$	Nitu$_2$(NCS)$_2$	Cdtu$_2$(NCS)$_2$	Selenourea	Cosu$_2$(NCS)$_2$	Nisu$_2$(NCS)$_2$	Cdsu$_2$(NCS)$_2$	Assignments†
3365 s	3395 s	3385 s	3375 s	3330 s	3380 sh	3375 s	3370 m	NH$_2$ stretch
3260 s	3365 s	3355 s	3290 s	3260 s	3365 s	3360 s	3285 s	
3165 s	3285 s	3280 s	3200 s	3150 s	3280 s	3280 s	3190 s	
3095 sh	3205 s	3200 s	3140 m	3085 sh	3200 s	3200 s	3130 m	
	3135 m	3135 m	2850 vw		3130 m	3130 m		
2680 w				2670 w,b	2235 vw			
				2165 vw				
	2078 vs	2088 vs	2068 vs		2070 vs	2082 vs	2058 vs	C–N stretch (NCS antisymmetric)
	2020 sh	2032 sh	2005 sh		2015 sh	2025 sh	1998 sh	
1632 sh	1638 vs	1638 vs	1638 vs	1638 sh	1631 vs	1636 vs	1624 vs	NH$_2$ bending
1589 vs	1621 sh	1621 sh	1630 vs	1612 vs	1618 sh	1618 sh	1634 vs	
				1604 vs				
1469 vs	1508 m	1510 m	1513 m	1483 m	1513 m	1516 m	1518 m	N–C–N stretch, NH$_2$ rocking, C=S or C=Se stretch
			1509 sh		1507 sh	1507 sh	1508 sh	
1432 s	1441 m	1442 m	1440 sh		1435 w	1440 w		N–C–N stretch, NH$_2$ rocking
	1415 m	1414 m	1421 m					
1387 m	1390 m	1387 m	1392 m	1398 s	1398 s	1400 s	1403 s	
1093 m	1102 vw	1105 vw	1110 vw	1090 m	1115 vw	1110 vw	1100 w,b	N–C–S bending overtone (NCS group)
	968 vw		968 vw					
	815 w	811 w	799 w		808 w	804 w	792 w	C=S stretch (NCS symmetric)
740 m	720 sh	720 sh	725 sh	732 w	720 w	724 vw	732 w	C=S or C=Se stretch, N–C–N stretch
723 m	702 m	699 m	704 m					
634 sh	600 m	598 w	605 m		624 w	623 w	628 sh	
620 m								
	560 s	560 s	556 s	560 s,b	569 s	570 s	591 m	N–C–N deformation
	527 s	530 s	538 sh		519 s	522 s	555 m	
487 s,b							522 m	
	482 w	481 w	483 w		479 w	480 vw	481 w	N–C–S bending (NCS group)
	471 vw	471 w	471 w		468 sh	467 vw	464 w	
	463 w	462 w	462 w					
408 sh	415 w	417 w	417 w	390 m	381 w	381 w	385 m	N–C–S deformation
	293 m	303 w			348 vw	330 vw		
	278 sh				291 vw	292 vw		

s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very.

* Registered by means of a Perkin–Elmer infrared spectrophotometer model 457 with the KBr disk technique.

† According to Yamaguchi, Penland, Mizushima, Lane, Curran & Quagliano, 1957; Kutzelnigg & Mecke, 1961; Collard-Charon & Renson, 1963.

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References

CHATT, J. & DUNCANSON, L. A. (1956). *Nature, Lond.* 178, 997.

COLLARD-CHARON, C. & RENSON, M. (1963). *Bull. Soc. chim. Belg.* 72, 149.

KUTZELNIGG, W. & MECKE, R. (1961). *Spectrochim. Acta,* 17, 530.

LEWIS, J., NYHOLM, R. S. & SMITH, P. W. (1961). *J. Chem. Soc.* p.4590.

MITCHELL, P. C. H. & WILLIAMS, R. J. P. (1960). *J. Chem. Soc.* p.1912.

NARDELLI, M., BRAIBANTI, A. & FAVA, G. (1957). *Gazz. Chim. Ital.* 87, 1209.

NARDELLI, M., FAVA GASPARRI, G., GIRALDI BATTISTINI, G. & DOMIANO, P. (1966). *Acta Cryst.* 20, 349.

NARDELLI, M., FAVA GASPARRI, G., MUSATTI, A. & MANFREDOTTI, A. (1966). *Acta Cryst.* 21, 910.

PECILE, C., GIACOMETTI, G. & TURCO, A. (1960). *R.C. Accad. Lincei* VIII, 28, 189.

PIOVESANA, O. & FURLANI, C. (1968). *J. Inorg. Nucl. Chem.* In the press.

SWAMINATHAN, K. & IRVING, H. M. N. (1964). *J. Inorg. Nucl. Chem.* 26, 1291.

YAGUPSKY, G., NEGROTTI, R. H. & LEVITUS, R. (1965). *J. Inorg. Nucl. Chem.* 27, 2603.

YAMAGUCHI, A., PENLAND, R. B., MIZUSHIMA, S., LANE, T. J., CURRAN, C. & QUAGLIANO, J. V. (1958). *J. Amer. Chem. Soc.* 80, 527.

# The crystal and molecular structure of dibromotetrapyrazolenickel(II), Ni(C₃H₄N₂)₄Br₂.

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The crystal and molecular structure of dibromotetrapyrazolenickel(II), Ni(C₃H₄N₂)₄Br₂, was determined by single-crystal X-ray diffraction techniques. Ni(C₃H₄N₂)₄Br₂ crystallizes in the monoclinic system with $a=14.127\pm0.007$, $b=9.334\pm0.003$, $c=14.702\pm0.002$ Å, $\beta=118.62\pm0.03°$, space group $C2/c$, $\varrho=1.94$ g.cm⁻³ and $Z=4$. The structure was found to be very similar to that of dichlorotetrapyrazolenickel(II). The R value based upon 2104 observed reflections is 0.081.

Introduction

In dichlorotetrapyrazolenickel(II), Ni(Pz)₄Cl₂, the pyrazole (I) rings lie nearly parallel to the Ni–Cl direction

(I)
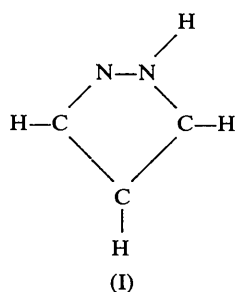
(Reimann, Mighell & Mauer, 1967) while in the related complex, dichlorotetrapyridinenickel(II), Ni(Py)₄Cl₂, the pyridine rings are inclined about 45° to the Ni–Cl direction (Porai-Koshits, 1954). In addition, the Ni–Cl distance is significantly longer in Ni(Pz)₄Cl₂ than in Ni(Py)₄Cl₂. Consequently the tetragonal distortion in the ligand field of the nickel ion is larger in the pyrazole complex than in the pyridine complex.

Dibromotetrapyridinenickel(II), Ni(Py)₄Br₂, has been investigated both structurally (Antsishkina & Porai-Koshits, 1958) and spectroscopically (Rowley & Drago,

1967). In view of the significant differences between the chloride complexes indicated above, dibromotetrapyrazolenickel(II), Ni(Pz)₄Br₂, was prepared so that it could be compared with the above compounds. Ni(Pz)₄Br₂ was found to have the same space group as Ni(Pz)₄Cl₂ with similar cell dimensions; this suggests that the gross structures are also similar. However, to compare these related complexes and to give a meaningful interpretation of their spectroscopic properties, it is necessary to determine bond distances and angles in the bromide complex. Therefore, the structure solution of Ni(Pz)₄Br₂ was undertaken.

Experimental and refinement

Crystals of Ni(Pz)₄Br₂ were grown from an aqueous solution of NiBr₂ and pyrazole. The crystal system and approximate cell parameters were determined from precession photographs taken with Cu Kα radiation ($\lambda=1.54051$ Å). The observed systematic absences are consistent with either Cc or $C2/c$. The centric space group was assigned on the basis of the complete structure determination. The 2θ angles of seventeen strong reflections in the range 20–45° were measured with a diffractometer using Mo Kα radiation ($\lambda=0.710688$ Å), and the cell parameters were refined by least-squares analysis. The density was determined by flotation in a mixture of chloroform and ethylene dibromide. The crystal data are given in Table 1. For comparison, the cell dimensions of the related chloride complex, Ni(Pz)₄Cl₂, are also given.