Crystal Structures of Bis(terpyridyl)cobalt(II) Thiocyanate Dihydrate: An *X*-Ray-induced Phase Transition?

By **Colin L. Raston** and **Allan H. White**,* Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

The crystal structures of two phases (I) and (II) of the title compound have been determined by *X*-ray diffraction and refined by least squares to R 0.12 (I) and 0.064 (II) for 1 136 and 660 observed reflections. Crystals of both forms are triclinic, $Z = 2$, space group $P\bar{1}$; (I) $a = 20.821(4)$, $b = 9.119(2)$, $c = 8.700(2)$ Å, $\alpha = 91.41(2)$, $\beta = 91.48(2)$, $\gamma = 101.69(2)$°; (II) $a = 20.71(1)$, $b = 9.036(5)$, $c = 8.746(3)$ Å, $\alpha = 91.11(4)$, $\beta = 91.17(4)$, $\gamma = 104.29(5)$°.

Phase (II) with unit cell volume 30 Å^3 less than for (I) appears to be produced by *X*-ray-stimulated phase transition, which is accompanied within the lattice by an ordering of one of the thiocyanate groups. The compound is a 'crossover' derivative and the central Co–N distances are longer (1.98 and 1.95 Å) than in the corresponding pseudo-isostructural bromide (1.89 Å) in which the proportion of the low-spin component is higher.

A RECENT *X*-ray crystallographic study aimed at defining the role of the anion as a determinant of the electronic crossover situations found in the salts of the bis(terpyridyl)cobalt(II) cation[1] has suggested that in the bromide, $[Co(terpy)_2]Br_2,3H_2O$, at room temperature the probable causational factor is either static disorder of one of the anions between different sites or a dynamic thermally stimulated interchange of the anion between two closely adjacent lattice sites of comparable energy;[2] in examining the temperature-dependence of the magnetic moments of the salts the former possibility might be expected to lead to hysteresis effects not observable with the latter. As an extension of this work a number of other previously described salts were prepared and examined; among these, the thiocyanate salt seemed particularly interesting initially because of the readiness with which large well-formed strongly-diffracting crystals were obtained by cooling a hot aqueous solution, and also because the unit cell was found to be similar in symmetry and dimensions to that of the bromide, in spite of a rather different room-temperature magnetic moment (*ca.* 4.0 *cf.* 2.9 B.M. for the bromide), suggesting the possibility of defining more closely the nature of the cation distortion associated with interconversion of ground state.

On closer examination, *i.e.* at the initiation of the data collection, the crystals were found to differ unexpectedly and remarkably from the bromide in that, although stable indefinitely in the atmosphere under normal conditions, they were found to undergo an irreversible phase-change after exposure to the *X*-ray beam for some time. The onset of this transition is sudden and very variable in the length of exposure necessary to precipitate it; among the specimens studied the time varied from 1 to 12 h exposure to a conventional Cu- or Mo-K_α monochromatic radiation source (40 kV, 20 mA normal-focus tube). The intensities of a number of standard reflections monitored during data collection remained constant until the onset of the phase change; thereafter, the cell volume rapidly fell by *ca.* 30 Å^3 to its new value, but the intensities of the standards varied rapidly and continuously over a prolonged period and did not stabilize on 'ageing' for a week in the beam; the orientation matrix of the crystal was, of course, also subject to change as the cell volume changed, but, in spite of the stability of the latter after a relatively short period, did not stabilize rapidly after the transition. The crystal otherwise showed no evidence of decomposition or degradation and diffracted *X*-rays strongly and continuously throughout the experiment; the reflection width did not change appreciably.

A large number of independent attempts were made to gather *X*-ray data sets on different crystals before the onset of the phase change, with wide variations in conditions of scan rate, background-time–scan-time ratios, radiation type, *etc.*, in an attempt to optimize the size, scope, and quality of the data set in the hope of obtaining a good, homogeneous, and extensive collection; this was made difficult by the unpredictable period of exposure before the phase change. The possibility of obtaining a data set on the phase formed after the transition point [phase (II)] was examined and abandoned because of the lack of stability of the crystal orientation and reflection intensity. However, it was found afterwards that one of the early trial data sets, which had been collected very rapidly and not seriously entertained, had, in fact, been collected on a crystal whose cell dimensions indicated it to be an apparently stable sample of phase (II) from the outset. Further attempts were made to locate crystals of phase (II) from the initially recrystallized phase (I) mixture but were unsuccessful, the phase apparently existing as a very minor impurity; repeated recrystallizations varying the conditions of formation were made but with no better success, and it has not been possible to obtain a better data set, nor, for that matter, to examine the physical properties of a pure stable sample of phase (II) in respect of magnetic moment, spectra, *etc.*

In spite of the limited accuracy imposed on the investigation of these structures by both lattice disorder and experimental conditions, due to the necessity of rapid data collection, it has been possible to solve the structure of both phases (I) and (II) and to determine

---

[1] J. S. Judge and W. A. Baker, *Inorg. Chim. Acta*, 1967, **1**, 68.

[2] E. N. Maslen, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1974, 1803.

the nature of the phase transition; the present paper describes this work. (The previously reported preparation describes the present salt as the monohydrate; the structure determination shows it to be the dihydrate, and, despite a number of examinations of a variety of recrystallized forms, no evidence has been found for the existence of a further phase. Such a result is not uncommon, as water analyses on hydrogen-containing derivatives of high molecular-weight are usually obtained by difference, as may have been the case in the present derivative, and tend to be very inaccurate.)

EXPERIMENTAL

The most extensive and accurate set of data from among the many collected on different crystals of phase (I) was obtained from a crystal closely approximating to a cube of side 0.35 mm; data collection was by a 2θ—θ scan using a Syntex $P\bar{1}$ four-circle diffractometer, with a scan rate of 4° min^{-1} and background counts on either side of the peak equal to 0.5 of the total scan time. Data were gathered within the limit $2\theta < 100°$ by use of Cu-K_α monochromatic radiation [$\lambda = 1.541\,8$ Å] for independent reflections only; a full hemisphere of data was not obtained, being terminated during the $h = 8$ sequence by the sudden onset of decomposition as evidenced by a rapid change in crystal orientation and standard intensities. Within these limits, 1 289 independent reflections were gathered, of which 1 136 having $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement after absorption correction.

For phase (II), as already described, only one time-independent data set was obtained from an apparently atypical crystal, a cuboid of side 0.20 mm. In this particular case, data were gathered for a full hemisphere within the limit $2\theta < 25°$ as before with scan rate 24° min^{-1} and a total background to scan time ratio of only 0.2, with Mo-K_α monochromatic radiation being used ($\lambda = 0.710\,69$ Å). Of 763 independent reflections 660 having $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement; no absorption correction was applied.

In both cases, cell calibrations were carried out by least-squares fit of the angular parameters of 15 reflections centred in the counter aperture; repeated determinations on the two phases were in good agreement.

Crystal Data [*for Phase* (I), *Data for Phase* (II) *in Parentheses*].—$C_{32}H_{26}CoN_8O_2S_2$, $M = 677.7$, Triclinic, $a = 20.821(4)$ [20.71(1)], $b = 9.119(2)$ [9.036(5)], $c = 8.700(2)$ [8.746(3)] Å, $\alpha = 91.41(2)$ [91.11(4)], $\beta = 91.48(2)$ [91.17(4)], $\gamma = 101.69(2)$ [104.29(5)]°, $U = 1\,616.4(7)$ [1 586(1)] Å^3, $D_m = 1.41(1)$, $D_c = 1.39$ (1.42), $Z = 2$, $F(000) = 682$. μ(Cu-K_α) 55.8 [μ(Mo-K_α) = 7.16 cm^{-1}]. Neutral atom scattering factors,[3] those for cobalt and sulphur being corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[4] Space group $P\bar{1}$ [but (I) may have a small acentric perturbation (see Discussion section)].

Patterson functions computed for both data sets confirmed the likely pseudo-isostructural nature of the complexes. Initial phasing of the solutions was carried out by use of the cobalt atom; the terpyridyl ligands were readily located and the structures refined carefully by least squares to enable location of water molecules and thiocyanate anions. In (II), solution of the full structure was straightforward; in (I), one of the water molecule oxygen atoms was found to be disordered over two sites. The relative populations could not be refined satisfactorily and they were ultimately fixed from a difference map. In (II), one of the thiocyanate anions is positioned close to a centre of symmetry at ($\frac{1}{2}$,$\frac{1}{2}$,0), the sulphur atoms being directed toward each other and separated by 3.82(1) Å, with very high thermal motion on the ligand carbon and nitrogen atoms. In (I), these thiocyanate anions are either disposed acentrically (but no reasonable acentric refinement of the structure was possible, *cf.* the bromide [2]) or are disordered. Only the sulphur atom could be located, much closer to the inversion image [2.77 (3) Å], and with very high thermal motion; carbon and nitrogen atoms could not be located. In view of the improbably close distance (the van der Waals' radius estimate of sulphur is 1.85 Å,[5]) the true description of the structure appears to be based *either* on a solution, basically centrosymmetric but with an acentric perturbation on these anions, or on a solution for which the present description of the thermal motion and/or disorder is a very poor approximation. As with the bromide, the intensity statistics of both (I) and (II) were indicative of a centrosymmetric structure, but this is only to be expected since the bulk, if not all, of the structure is basically centric.

Final refinement cycles were by 9 × 9 block-diagonal least-squares, the parameters of the CoN_6 cationic cores being refined jointly as a single block in an attempt to approximate to a full-matrix procedure. Hydrogen atoms were not located in either structure. In (II), only the cobalt, anions, and water oxygen atoms could be refined anisotropically, while, in (I), this was so for the cobalt, anion sulphur, and non-disordered water oxygen atoms; the form used was $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. At convergence in both cases no parameter shift exceeded 0.4σ, R being 0.12 (I) [0.064 (II)] and $R'[= (\Sigma\omega||F_o| - |F_c||^2/\Sigma\omega|F_o|^2)^{\frac{1}{2}}]$ 0.15 (I) [0.070 (II)]. Weighting schemes of the form $w = [\sigma^2(F_o) + 4 \times 10^{-4}(F_o)^2]^{-1}$ were found appropriate in both cases. The higher residuals obtained for (I) are considered to be a reflection of the disorder or acentricity present in that structure (*cf.* the bromide).[2]

Data processing and computation was carried out on a CDC 6 200 machine at this University with a local adaptation of the '*X*-ray 72' system.[6] Structure amplitudes together with a table of least squares planes are deposited as Supplementary Publication No. SUP 21401 (8 pp., 1 microfiche)*. The ligand numbering is shown in the formula: the atom number is preceded by kl where necessary in the Tables and Discussion, k being the ligand number (1 or 2) and l denoting the half of the ligand referred to (a or b) where non-unique atoms are involved. Final atomic and thermal parameters are listed in Table 1.

DISCUSSION

A comparison of the cell diagram (Figure) with that for the bromide shows a similarity between the two deriva-

---

* For details, see Notice to Authors, No. 7, Index issue, *J.C.S. Dalton*, 1975.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[5] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

[6] 'The *X*-Ray System, Version of June 1972,' Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

TABLE 1

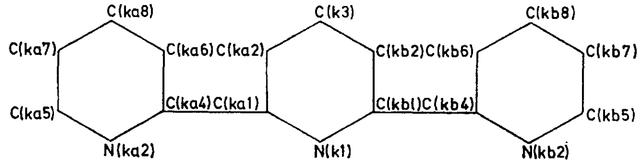
Atomic fractional cell ($x, y, z \times 10^4$ for Co, $\times 10^3$ for others) and thermal parameters ($\times 10^3$ Å^2) with least-squares estimated standard deviations in parentheses. Values for (II) follow those for (I)

Atom	x	y	z	U
The cation				
Co	2 474(4), 2 506(2)	4 576(4), 4 907(5)	3 511(4), 3 456(4)	*
(i) Ligand k = 1, unique atoms				
N(1)	150(1), 153(1)	389(2), 431(2)	318(2), 322(2)	65(6), 38(7)
C(3)	019(2), 019(1)	316(3), 337(3)	261(3), 276(3)	119(11), 106(12)
(ii) Ligand k = 1, part a				
N(2)	240(1), 245(1)	237(2), 263(2)	261(2), 264(2)	70(6), 60(8)
C(1)	126(1), 123(1)	247(2), 278(3)	249(2), 261(3)	79(8), 58(10)
C(2)	054(2), 053(1)	215(3), 233(3)	219(3), 228(3)	110(9), 84(11)
C(4)	180(1), 179(1)	176(2), 211(3)	224(2), 228(3)	65(7), 51(9)
C(5)	299(1), 290(1)	185(3), 178(3)	252(3), 227(3)	90(9), 86(11)
C(6)	167(2), 152(1)	019(3), 062(3)	153(3), 159(3)	107(9), 74(10)
C(7)	285(2), 265(1)	012(3), 030(3)	177(3), 164(3)	117(11), 64(9)
C(8)	220(1), 198(1)	−038(2), −020(3)	139(2), 129(3)	78(8), 77(10)
(iii) Ligand k = 1, part b				
N(2)	214(1), 222(1)	649(2), 689(2)	434(2), 429(2)	68(6), 81(9)
C(1)	106(1), 112(1)	478(2), 530(3)	353(2), 367(3)	60(7), 64(10)
C(2)	036(2), 043(1)	444(4), 482(3)	320(4), 330(3)	157(14), 82(11)
C(4)	149(1), 159(1)	623(2), 665(3)	421(2), 424(3)	69(8), 91(11)
C(5)	256(1), 267(1)	775(2), 814(3)	494(2), 490(3)	52(7), 55(10)
C(6)	109(2), 126(1)	745(3), 783(3)	461(3), 470(3)	117(11), 51(9)
C(7)	218(1), 238(1)	890(2), 934(3)	550(2), 550(3)	74(8), 81(11)
C(8)	150(1), 170(1)	866(3), 922(3)	529(3), 539(3)	102(9), 64(10)
(iv) Ligand k = 2, unique atoms				
N(1)	342(1), 346(1)	541(2), 567(2)	381(2), 367(2)	63(6), 49(7)
C(3)	469(1), 480(1)	680(3), 689(3)	438(3), 410(2)	94(9), 35(9)
(v) Ligand k = 2, part a				
N(2)	263(1), 267(1)	381(2), 418(2)	573(2), 575(2)	64(6), 74(8)
C(1)	373(1), 381(1)	521(2), 553(3)	520(2), 506(3)	74(8), 43(9)
C(2)	437(1), 447(1)	597(3), 607(3)	551(3), 528(3)	89(9), 94(12)
C(4)	326(1), 333(1)	423(2), 457(3)	616(2), 600(3)	54(7), 59(10)
C(5)	214(1), 219(1)	289(2), 325(3)	653(2), 656(3)	64(7), 57(9)
C(6)	355(1), 358(1)	374(3), 409(3)	758(3), 743(3)	92(9), 65(10)
C(7)	234(1), 246(1)	233(2), 281(3)	794(2), 804(3)	77(8), 71(10)
C(8)	302(1), 310(1)	273(2), 313(3)	840(2), 844(3)	77(8), 81(11)
(vi) Ligand k = 2, part b				
N(2)	269(1), 275(1)	559(2), 591(2)	137(2), 136(2)	55(6), 72(9)
C(1)	376(1), 384(1)	627(2), 654(3)	270(2), 254(3)	62(7), 54(9)
C(2)	440(1), 454(1)	696(3), 711(3)	301(3), 268(3)	84(9), 53(9)
C(4)	333(1), 340(1)	631(2), 660(3)	133(2), 116(3)	60(7), 65(10)
C(5)	228(1), 228(1)	561(2), 597(3)	018(2), 022(3)	61(7), 74(10)
C(6)	359(1), 368(1)	715(2), 753(3)	002(2), −004(3)	72(8), 88(11)
C(7)	251(1), 254(1)	647(2), 676(3)	−115(2), −117(3)	62(7), 71(10)
C(8)	316(1), 320(1)	717(2), 758(3)	−119(2), −120(3)	70(8), 56(10)
(vii) The anions				
S(1)	043(1), 041(1)	157(1), 153(1)	714(1), 701(1)	*
C(1)	063(2), 060(2)	315(3), 300(5)	792(3), 785(4)	146(13) *
N(1)	078(2), 083(1)	421(4), 408(3)	834(4), 848(3)	228(15) *
S(2)	469(1), 459(1)	376(2), 314(1)	078(2), 097(1)	*
C(2)	448(2)	145(4)	205(3)	*
N(2)	452(2)	071(4)	287(4)	*
(viii) The water oxygens				
O(1)	083(1), 080(1)	694(2), 688(3)	033(2), 023(2)	*
O(21) †	390(1), 416(9)	014(3), 970(2)	582(3), 595(2)	129(10) *
O(22) †	419(3)	000(6)	734(6)	109(21)

* Anisotropic thermal parameters of the cobalt, anions, and water molecules. † Populations: O(21), 0.700; O(22), 0.300 [(I) only; see text].

Atom		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	(I)	93(8)	41(3)	46(3)	16(3)	3(2)	2(2)
	(II)	49(4)	72(4)	39(4)	17(3)	−3(3)	4(3)
S(1)	(I)	74(14)	125(8)	323(14)	−24(8)	23(10)	−5(8)
	(II)	84(9)	144(11)	311(16)	33(8)	15(10)	19(11)
C(1)	(II)	126(36)	234(45)	207(45)	27(34)	−35(32)	−86(36)
N(1)	(II)	83(24)	222(33)	20(32)	51(24)	−60(22)	−54(26)
S(2)	(I)	239(25)	592(36)	228(17)	188(23)	−90(14)	−166(17)
	(II)	101(9)	197(11)	81(8)	46(8)	1(7)	2(8)
C(2)	(II)	144(35)	169(37)	98(31)	47(30)	−38(26)	−18(27)
N(2)	(II)	347(50)	236(40)	206(37)	148(38)	−54(34)	12(31)
O(1)	(I)	82(27)	169(19)	153(18)	27(17)	−26(15)	−16(14)
	(II)	155(23)	156(23)	143(22)	18(18)	−30(18)	−25(18)
O(21)	(II)	61(17)	75(17)	175(22)	−44(14)	−1(15)	2(16)

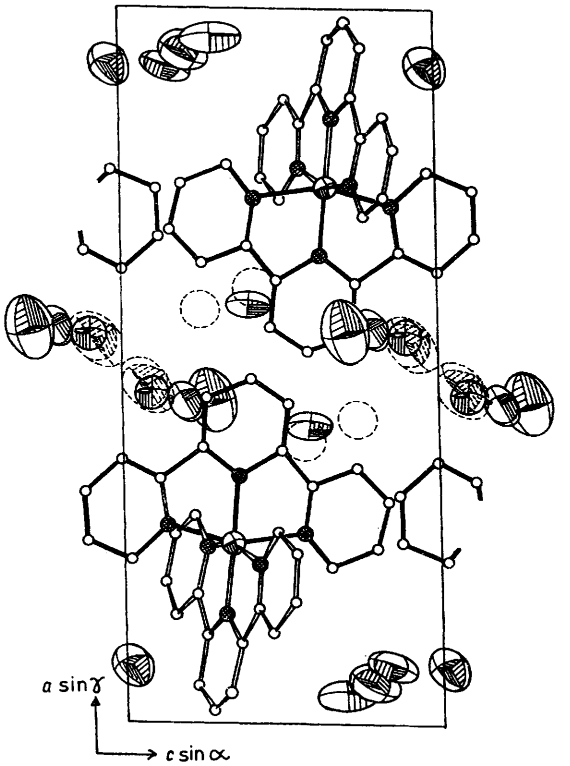
tives which extends beyond the similarity of the cell dimensions although it would be carrying the analogy too far to say that the complexes are isostructural. In both bromide and thiocyanate complexes, the complex cations are centred on cobalt atoms disposed very near the plane $x = 0.25$, with the two ligand planes lying approximately parallel to the *ab* and *ac* planes. In the bromide, the ordered anion and the two ordered water molecules lie close to the plane $x = 0$, while in the thiocyanate a similar situation is found, the ordered water molecule and thiocyanate anion (replacing a bromide and a water molecule), also lying close to $x = 0$. In (I) and the bromide, in the two cases, a disordered water molecule and anion lie near the plane $x = 0.5$. The similarity of x co-ordinates extends to the individual atoms of the two for both derivatives. However, the comparison does not extend to the y and z co-ordinates; similarities exist for some of the species, particularly if y and z are interchanged but for others no relationship appears to exist.



Phases (I) and (II) of the thiocyanate are clearly closely related; the common disordered phase (I) on conversion to the ordered phase (II) is accompanied by a cell contraction of 30 $Å^3$. As with the bromide, the electronic properties are indicative of a ground-state equilibrium, the thiocyanate containing rather more of the high-spin component than the bromide. The electronic anomaly can, by analogy with the bromide, be explained in terms of either a static or dynamic disorder of the thiocyanate anion although in the present case the relative populations of the two components of the disorder cannot be established nearly as well as in the bromide. [While there appear to be two components of the disordered water molecule, this may not be true of the thiocyanate which is very poorly defined and may comprise an acentric atomic distribution (see earlier).] If the relative populations are taken as 0.3 and 0.7, the result is approximately consistent with the observed magnetic moment of 4.0 B.M. using a similar model to that used in the bromide.

In this context a comparison of the metal–ligand geometry (Table 2) is rewarding; although the accuracy is low [and this may account for the fact that the properties of phase (II) do not lie monotonically between those of phase (I) and the bromide] it is very probable that the transition from low- to high-spin is accompanied by an elongation primarily of the central nitrogen–metal bond, the peripheral nitrogen–metal distance remaining relatively constant. Since both complexes studied are spin-mixed, it is likely that the difference between pure low- and high-spin geometries may be considerable, involving a central nitrogen–cobalt distance change of >0.1 Å. The associated angular geometry about the cation core appears very sensitive to the change in spin-state also; while there is no appreciable change apparent in the CoN_6 core angular geometry, the angles at the pyridine–pyridine bridges and also at the peripheral nitrogen change considerably as might be expected.

While such a change in metal–ligand distance may be regarded as unduly large considering that the transition is doublet–quartet involving the unpairing of only one electron, it should be noted that in either the O_h or $D_{\infty h}$ extreme approximations (*i.e.* six-co-ordinate or two-co-ordinate) the orbital of highest energy will be directed along the metal–central-nitrogen axis and any change in spin-state must necessitate its occupation. [In the three structures, all cases depart significantly from the ideal co-ordination with N(11)–Co–N(21) 180°, the angle being reduced to 176 ± 1°.]



Unit-cell contents projected down *b*; solid lines indicate the structure of the ordered phase (II) showing 50% thermal ellipsoids of the cobalt, SCN, and water oxygen atoms. The structure of (I) is similar: dotted lines show the position of those atoms which are disordered with respect to the phase (II) solution; a thermal ellipsoid is given for the sulphur atom, the C and N atoms not being located, and the disordered water oxygen being refined isotropically. The projection is not the same as that of the bromide (ref. 2) and is intended to show the relationship of the disordered anions more clearly. Ligand 2 is shown with solid bonds and, as with the bromide, is defined so as to be the ligand directed toward the centre of the cell

It has been suggested that, for the bromide, the mechanism controlling the crossover is interaction of the disordered species with ligand (2), effecting a corresponding distortion on the core of the cation, affecting both metal–ligand σ and π bonds. In the bromide and the present examples, it is found that the ligands are in fact considerably distorted in all three structures; angles between adjacent pyridine rings in any one ligand may be as high as 10° and deviations of the cobalt atom from the pyridine plane as much as 0.23 Å. In the bromide, the greatest ligand distortions appear to be associated with ligand (1), but in the thiocyanate these occur in ligand (2). The change from phase (I) to (II) in the thiocyanate appears to be accompanied by some relief of intraligand strain; whereas distortion within ligand (1) is small and remains so in both (I) and (II), distortion in ligand (2) is large in (I), the angles between adjacent ring planes being 9.9 and 4.3° falling to 6.7 and 3.8° on passing to phase (II).

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses. Values for (II) follow those for (I)

(*a*) Cation geometry

(i) Cation core

Co–N(11)	2.00(2), 1.97(2)	Co–N(21)	1.96(2), 1.93(2)
C(1a1)–N(11)–C(1b1)	118(2), 121(2)	C(2a1)–N(21)–C(2b1)	120(2), 115(2)
C(1a2)–C(13)–C(1b2)	131(3), 129(3)	C(2a2)–C(23)–C(2b2)	122(3), 127(2)
N(11)–Co–N(2a2)	102.1(7), 102.3(8)	N(1a2)–Co–N(2a2)	89.3(6), 88.5(8)
N(11)–Co–N(2b2)	98.6(7), 99.7(8)	N(1a2)–Co–N(2b2)	94.1(6), 95.2(8)
N(21)–Co–N(1a2)	106.2(8), 100.1(8)	N(1b2)–Co–N(2a2)	93.9(7), 92.5(8)
N(21)–Co–N(1b2)	96.7(8), 98.8(8)	N(1b2)–Co–N(2b2)	90.8(7), 91.1(8)
N(1a2)–Co–N(1b2)	157.2(8), 160.9(8)	N(2a2)–Co–N(2b2)	159.3(8), 157.9(8)
N(11)–Co–N(21)	175.6(8), 175.1(8)		

(ii) Ligand fragment

k1	1a	1b	2a	2b
Co–N(2)	2.12(2), 2.14(2)	2.12(2), 2.14(2)	2.11(2), 2.17(2)	2.12(2), 2.07(2)
N(1)–C(1)	1.40(3), 1.45(3)	1.39(4), 1.43(3)	1.39(3), 1.43(3)	1.38(3), 1.41(3)
N(2)–C(4)	1.28(3), 1.36(3)	1.33(3), 1.26(3)	1.33(3), 1.34(3)	1.37(3), 1.37(3)
N(2)–C(5)	1.41(4), 1.39(4)	1.38(2), 1.38(3)	1.39(3), 1.35(3)	1.33(3), 1.39(3)
Co–N(1)–C(1)	119(2), 117(2)	123(1), 122(1)	120(2), 122(1)	121(2), 122(2)
Co–N(2)–C(4)	111(2), 102(2)	109(1), 110(2)	110(1), 106(2)	112(1), 117(2)
Co–N(2)–C(5)	116(1), 136(1)	123(2), 122(2)	123(1), 124(2)	128(1), 124(2)
N(1)–Co–N(2)	77.7(8), 84.3(8)	79.5(8), 76.8(8)	80.2(7), 80.0(8)	79.2(7), 78.0(8)
C(4)–N(2)–C(5)	132(2), 102(2)	128(2), 128(2)	126(2), 129(2)	121(2), 120(2)
C(1)–C(4)	1.43(4), 1.45(4)	1.54(3), 1.43(3)	1.48(3), 1.44(3)	1.48(3), 1.51(3)
C(1)–C(2)	1.48(4), 1.44(4)	1.44(4), 1.43(4)	1.39(4), 1.33(3)	1.37(4), 1.42(3)
C(2)–C(3)	1.34(5), 1.38(4)	1.24(4), 1.35(4)	1.36(3), 1.38(3)	1.35(3), 1.38(3)
C(4)–C(1)–N(1)	108(2), 106(2)	104(2), 104(2)	108(2), 105(2)	110(2), 109(2)
C(4)–C(1)–C(2)	138(2), 134(2)	129(2), 139(3)	131(2), 130(2)	131(2), 128(2)
N(1)–C(1)–C(2)	114(2), 119(2)	127(2), 117(2)	120(2), 124(2)	119(2), 123(2)
C(1)–C(2)–C(3)	120(2), 114(2)	111(3), 118(3)	118(2), 116(2)	121(2), 114(2)
C(4)–C(6)	1.51(3), 1.44(3)	1.56(4), 1.46(4)	1.48(3), 1.46(4)	1.44(3), 1.39(4)
C(5)–C(7)	1.66(4), 1.41(3)	1.52(4), 1.47(4)	1.43(3), 1.50(4)	1.45(3), 1.47(3)
C(6)–C(8)	1.32(4), 1.37(4)	1.36(4), 1.47(3)	1.49(3), 1.46(3)	1.37(3), 1.41(4)
C(7)–C(8)	1.36(4), 1.37(4)	1.32(4), 1.38(4)	1.42(4), 1.34(4)	1.37(3), 1.40(3)
N(2)–C(4)–C(1)	124(2), 130(2)	125(2), 121(2)	122(2), 127(2)	118(2), 114(2)
N(2)–C(4)–C(6)	118(2), 122(2)	123(2), 121(2)	124(2), 117(2)	122(2), 127(2)
C(1)–C(4)–C(6)	119(2), 108(2)	113(2), 111(2)	115(2), 116(2)	120(2), 118(2)
N(2)–C(5)–C(7)	116(2), 118(2)	111(2), 114(2)	116(2), 113(2)	119(2), 116(2)
C(4)–C(6)–C(8)	114(2), 115(2)	109(3), 115(2)	109(2), 119(2)	116(2), 113(2)
C(5)–C(7)–C(8)	111(3), 119(3)	121(2), 122(2)	118(2), 124(2)	120(2), 120(2)
C(6)–C(8)–C(7)	134(2), 125(2)	128(3), 119(2)	127(2), 118(2)	122(2), 123(2)

(*b*) The anion

(1) N–C	1.01(4), 1.10(5)	C–S	1.54(3), 1.47(4)
	S–C–N	175(3), 170(4)	
(2) [(II) only]	N–C 1.00(5)	C–S	1.78(3)
	S–C–N	163(3)	

(*c*) Intermolecular contacts <3.0 Å (for NCS · · · SCN contacts, see text)

O(1) · · · N(1)	2.98(4), 2.95(4)	O(2) · · · N(2)	?, 2.91(4)

(*d*) Relevant geometrical parameters for the bromide [2] for comparison

⟨Co–N(1)⟩	1.89	⟨N(2)–C(4)–C(1)⟩	114	⟨N(2)–Co–N(1)⟩	79.2
⟨Co–N(2)⟩	2.10	⟨Co–N(1)–C(1)⟩	121	⟨N(2)–Co–N(2)⟩	158.3
⟨N(1)–C(1)–C(4)⟩	112.5	⟨Co–N(2)–C(4)⟩	113	⟨N(11)–Co–N(21)⟩	176.3

The mechanism of the transition remains obscure; it is clear that it requires (*a*) passage of time, and (*b*) probably the presence of thiocyanate ions, rather than, say, bromide ions. It appears unlikely that the effect involves the production of an excited state involving *e.g.* bent thiocyanate ions which might precipitate a co-operative lattice effect since one would expect the (very small?) steady-state concentration of excited species to be achieved almost instantaneously. A more likely explanation is that the effect is triggered by the gradual build-up of a small amount of decomposition product within the lattice: the continued growth of such impurities after the transition would perhaps account for the stable cell dimensions of phase (II), but not the instability of the reflection intensities, although it is clear that the predominant part of the lattice must persist for a very long time. Photochemical interactions between thiocyanate and water are well established [7] (and for that matter for bromide and water also) and the proximity of both water molecules to the thiocyanate anions in the present system is very apparent (Table **3**), suggesting that an interaction of this type may be responsible.

The anion geometries in both structures are inaccurate and unexceptional.

[5/221 *Received*, 3*rd February*, 1975]

---

[7] E. Gusarsky and A. Treinin, *J. Chem. Phys.*, 1965, **69**, 3176, and refs. therein.