Inorganica Chimica Acta, *87* (1984) 19–24

Tetrakis (2-aminothiazole) *trans* bis-(N-thiocyanato) Cobalt(II): Spectroscopy, Thermal Analysis and Crystal Structure

E. S. RAPER*, J. R. CREIGHTON, R. E. OUGHTRED

School of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne, NE1 8ST, U.K.

and I. W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Sheffield, S1 1WB, U.K.

Received November 17, 1983

*The reaction between 2-aminothiazole (2-*amt*) and $Co(NCS)_2 \cdot 6H_2O$ in absolute ethanol produces $Co(2\text{-amt})_4(NCS)_2$. The stoichiometry of the complex has been established by a combination of chemical (C,H,N), thermal and X-ray analyses. The complex is monomeric in the solid with a distorted CoN_6 octahedron and Co–N(av) distances of 2.182 Å to the hetero N-atoms of 2-*amt *and 2.113 Å to the thiocyanate N-atoms. The average Co–NC(S) angle is 160.2°. The infrared and electronic absorption spectra are also consistent with N-donation by both ligands. The complex autocatalytically decomposes on heating in nitrogen.*

Introduction

The molecule 2-aminothiazole (2-*amt*) (Fig. 1) exhibits *amino–imino* tautomerism and has a coordination potential which includes monodentate sulphur, flexidentate nitrogen and in the deprotonated form, amidine N,N-bridging.

Solution studies with various metals (M(II) = Mn, Co, Ni, Cu and Zn) have shown that 1:1 and 1:2 (metal:ligand) complexes are formed in acid media [1]. Binding through the amino nitrogen atom has been proposed for all the above metals except for copper where the interaction is believed to occur through the heterocyclic sulphur atom. With nickel halides and perchlorates, complexes of formulae $[Ni(2\text{-amt})_4X_2]$ are produced and coordination is proposed to occur through the amino nitrogen [2]. With cobalt, nickel and copper salts tetrahedral, tetragonal and polymeric octahedral geometries are proposed with the ligand coordinating through its heterocyclic nitrogen and possibly by means of its amino nitrogen in $[Ni(2\text{-amt})_4(NCS)_2]$ [3]. In another report dealing with the complexes of metal thiocyanates and 2-*amt* it has been suggested that heterocyclic sulphur is the donor atom with cobalt, nickel and zinc with the anion nitrogen bonded [4].

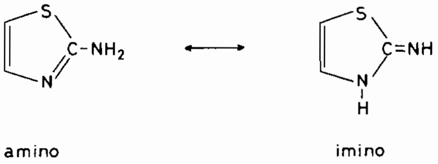

Fig. 1. Tautomeric forms of 2-*amt*.

X-ray studies have shown that the exocyclic amino group is conjugated to the thiazole molecule in the 4-phenyl derivative of 2-*amt* [5]. Similar conjugation exists in complexed 2-*amt* molecules which are hetero-nitrogen bonded in pseudo-tetrahedral $[Co(2\text{-amt})_2Cl_2]$ [6].

In view of the sulphur coordination proposed for 2-*amt* in $[Co(2\text{-amt})_4(NCS)_2]$ [4] we have undertaken a spectroscopic, structural and thermal analysis study of this complex.

Experimental

Starting Materials

The ligand was obtained from the Aldrich Chemical Company. The remaining chemicals were of reagent quality and were supplied by Phase Separation Ltd.

Analyses

C, H and N were analysed by Butterworths Microanalytical Services Ltd., Teddington, Middlesex.

Preparation

The complex $[Co(2\text{-amt})_4(NCS)_2]$ was prepared by refluxing hydrated cobalt thiocyanate (1 m.mol) and 2-*amt* (4 m.mol) in absolute ethanol (50 cm^3), in the presence of triethylorthoformate, for one

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Crystallographic Data.

Compound	$CoC_{14}H_{16}N_{10}S_6$
M_r	575.5
a, Å	10.640(3)
b, Å	13.070(4)
c, Å	16.942(4)
α, γ, deg	90.0
β, deg	91.78(2)
U, Å^3	2354.8 Å^3
Z	4
D_c, g cm^{-3}	1.63
D_m, g cm^{-3}	1.60(1)
space group	$P2_1/n$
radiation, Å	MoKα, 0.71073
$F(000)$	1172
μ, cm^{-1}	12.05
diffractometer	Enraf-Nonius CAD-4
2θ range, deg	3.8–50.0
scan mode	$\theta-2\theta$
total data	4138
$F_o^2 \geqslant 3\sigma(F_o^2)$	3273
R	0.0441
R_w	0.0542
w	$1.0000/[(\sigma^2)F_o + 0.004200\,F_o^2]$

hour. The reaction mixture was filtered hot and set aside overnight during which pale-pink crystals developed. These were removed by filtration washed with cold absolute ethanol and vacuum dried. Chemical analysis gave (calc. (obs)) C, 29.2(29.15)%; H, 2.8 (2.83)%; N, 24.3(24.48)% and confirmed the stoichiometry, $Co(2\text{-amt})_4(NCS)_2$.

Physical Measurements

Infrared spectra of 2-*amt* and $[Co(2\text{-amt})_4(NCS)_2]$ were obtained as CsI discs in the range 4000–200 cm^{-1} from a PERKIN-ELMER 577 grating spectrophotometer. Solid state diffuse electronic spectra of the complex were obtained from a CARY 17D spectrophotometer in the range 350 to 2600 nm. Magnetic measurements were performed at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as standard. Molecular Susceptibilities were corrected for the diamagnetism of the component atoms by means of Pascal's constants. Thermal analysis curves (TG, DTG and DTA) were obtained from Stanton-Redcroft TG 750 and DTA 673/4 instruments. Sample masses were in the range 2–7 mg and heating rates were 10 or 20 °C min^{-1}. Platinum crucibles were used for the TG results and 3 cm quartz crucibles for the DTA results. Gas flow rates were 5 cm^3 min^{-1} for the TG (air) and 200 cm^3 min^{-1} (nitrogen) for the DTA. Calibration details for the quantitative DTA data are reported elsewhere [7].

TABLE II. Non-H Atoms Final Fractional Coordinates (×10^4) with e.s.d.'s in Parentheses and B_{eq} [16].

	x	y	z	B_{eq} (Å^2)
Co	−135(0)	242(0)	2411(0)	2.63(2)
S(1)	3145(1)	866(1)	4380(1)	4.63(5)
C(1)	1959(3)	845(3)	3752(2)	3.0(1)
N(1)	1091(3)	811(2)	3318(2)	3.4(1)
S(2)	−3409(1)	−1318(1)	798(1)	7.60(8)
C(2)	−2181(4)	−788(3)	1220(2)	3.9(2)
N(2)	−1325(3)	−414(3)	1533(2)	4.1(2)
S(11)	481(1)	3155(1)	851(1)	4.90(5)
C(21)	108(4)	1891(3)	1065(2)	3.9(2)
N(31)	−5(3)	1700(2)	1812(2)	3.2(1)
C(41)	179(3)	2592(3)	2248(2)	3.5(2)
C(51)	453(4)	3424(3)	1844(2)	4.3(2)
N(21)	−29(4)	1164(3)	493(2)	6.0(2)
S(12)	−602(1)	−2509(1)	4174(1)	5.59(5)
C(22)	−1052(4)	−1658(3)	3426(3)	4.4(2)
N(32)	−137(3)	−1207(2)	3086(2)	3.3(1)
C(42)	1018(4)	−1562(3)	3415(2)	4.1(2)
C(52)	929(4)	−2254(3)	3989(2)	4.8(2)
N(22)	−2290(3)	−1503(3)	3215(3)	5.8(2)
S(13)	−3630(1)	957(1)	3936(1)	4.72(5)
C(23)	−2057(4)	776(3)	3746(2)	3.4(1)
N(33)	−1788(2)	805(2)	2994(2)	3.0(1)
C(43)	−2871(3)	1027(3)	2540(2)	3.6(1)
C(53)	−3940(4)	1122(3)	2936(2)	4.3(2)
N(23)	−1200(3)	595(3)	4337(2)	4.6(2)
S(14)	3151(1)	−1214(1)	982(1)	4.67(5)
C(24)	1699(3)	−1110(3)	1415(2)	3.3(1)
N(34)	1519(3)	−264(2)	1796(2)	3.1(1)
C(44)	2576(3)	379(3)	1750(2)	3.7(2)
C(54)	3537(4)	−16(3)	1342(3)	4.6(2)
N(24)	833(3)	−1876(3)	1327(2)	4.6(2)

Crystal Structure Analysis

Relevant crystal data are listed in Table I; the intensity data were corrected for Lorentz, polarisation and absorption effects. The cobalt atom coordinates were obtained by a combination of Patterson and direct methods procedures. The remaining atoms were located by difference-Fourier methods. The coordinates of all non-H atoms were refined by full-matrix least squares analysis with anisotropic temperature factors. Ethylenic H-atoms were given idealised geometry (C–H = 1.08 Å) and a common isotropic temperature factor (U = 0.073(10) Å^2). Attempts to locate the amino H-atoms were unsuccessful. Scattering factors for all atoms were calculated from an analytical approximation [8]. Final atomic parameters are in Table II.

All calculations were performed on the NUMAC, IBM 370/168 computer at the University of Newcastle upon Tyne. SHELX [9] and related programs

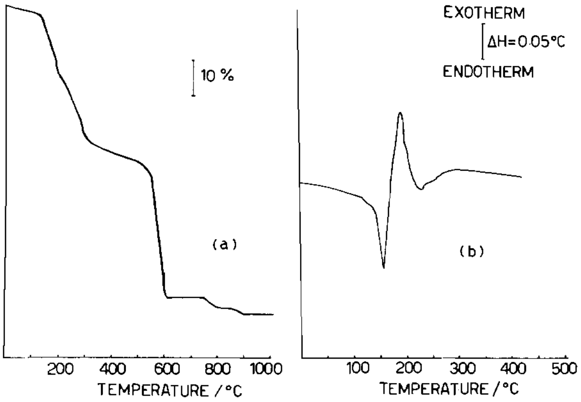

Fig. 2. Thermal Analysis Curves (a) TG (b) DTA of the complex.

were used in the analysis [Anisotropic temperature factors, H-atom coordinates as well as observed and calculated structure factors have been deposited with the Editor].

Results and Discussion

The room temperature magnetic moment (5.20 B.M.) and the pale pink appearance suggests the complex to contain six coordinate cobalt(II).

The diffuse reflectance spectrum consists of a charge transfer band (20,000 cm^{-1}) and two d–d absorptions. The ν_2 band ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) at 19,231 cm^{-1} appears on the low-energy side of the charge transfer band. The ν_1 band at 9.091 cm^{-1} ($^4T_{1g}(F) \rightarrow {}^4T_{2g}$) is broad and relatively weaker than ν_1. The ν_2/ν_1 ratio (2.11) agrees with the theoretical value (2.1–2.2) for octahedral cobalt(II) and confirms the assignment [10]. Calculation of Dq (1014 cm^{-1}) [11] suggests a relatively large ligand field strength consistent with a $[CoN_6]$ chromophore. The value of B′ (501 cm^{-1}) was obtained from a graphical correlation of the ν_2/ν_1 ratios and Dq/B values [10] and is rather low. In a previously reported study of the complex Dq is given as 1022 cm^{-1} and B′, obtained from a ν_3/ν_2 ratio is 656.4 cm^{-1} [4].

The infrared spectrum of the complex shows a broad and intense band in the region 3500–3200 cm^{-1} which is a composite of ν_s(NH) and ν_{as}(NH). This contrasts with weak absorption at 3400, 3280 and 3150 cm^{-1} in the free 2-*amt* molecule. Lowering of the ν(CN) band from 1625 cm^{-1} in the free molecule to 1600 cm^{-1} in the complex is consistent with heterocyclic N-donation to the metal. The ν(C–S) activity in the free molecule consists of an absorption of moderate intensity at 690 cm^{-1} with an associated shoulder at 705 cm^{-1}. These are replaced by an absorption of increased intensity at 720 cm^{-1} with associated peaks at 710 and 695 cm^{-1}. Positive shifts of this character are not usually indicative of S-donation but the implication is that some perturbation of the 'thioamido' portion of the heterocycle occurs upon coordination. The presence of ν(C–N) at 2020 and 2040 cm^{-1} and δ(NCS) at 480 cm^{-1} are consistent with N-donation by the anion [12]. The infrared spectrum of the complex is consistent with a CoN_6 coordination sphere.

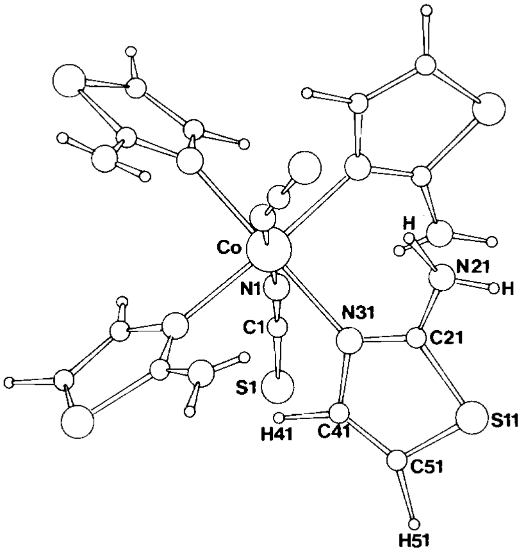

Fig. 3. Perspective view of the complex with atomic labelling and amino hydrogens in calculated positions.

The complex thermally degrades to CoO over the temperature range 120–1000 °C (Fig. 2(a)). Observed (87.0%) and theoretical (87.0%) mass losses are within experimental error (±2.0%). The mass loss in the temperature range 120–180 °C (37.0%) is consistent with the removal of two 2-*amt* molecules (theor. 35.0%). The remaining two organic molecules are lost very rapidly between 580–600 °C.

Between these two stages (180–580 °C) a slow mass loss (10%) is observed which is consistent with the evolution of cyanogen from the thiocyanate group (theor. 9.5%).

Infrared spectra of the deposits at various stages showed a significant loss of intensity among the bands due to the organic ligand at 200 °C but a clear retention of vibrational activity due to the thiocyanate anion. At 400 °C diminution of thiocyanate band intensity occurred. At higher temperatures the products became increasingly contaminated with residual carbon and the spectra were inconclusive. Between 600 and 1000 °C the residual sulphide is progressively converted to Co_3O_4 and CoO.

The differential thermal analysis curve in nitrogen Fig. 2(b), consists of an endotherm (T_p = 164 °C) followed by an exotherm (T_p = 192 °C). The reaction

TABLE III. Bond Lengths (A) and Angles (°) with e.s.d's in Parentheses.

(a) *The coordination sphere*

Co–N(1)	2.119(3)	N(1)–Co–N(31)	89.1(1)
Co–N(2)	2.106(3)	N(1)–Co–N(32)	86.3(1)
Co–N(31)	2.165(3)	N(1)–Co–N(33)	92.3(2)
Co–N(32)	2.213(3)	N(1)–Co–N(34)	88.0(2)
Co–N(33)	2.173(3)	N(1)–Co–N(2)	176.5(1)
Co–N(34)	2.176(3)	N(2)–Co–N(31)	94.2(1)
		N(2)–Co–N(32)	90.4(1)
		N(2)–Co–N(33)	88.9(2)
		N(2)–Co–N(34)	90.9(2)
		N(31)–Co–N(32)	175.3(1)
		N(31)–Co–N(33)	88.8(2)
		N(31)–Co–N(34)	88.8(2)
		N(32)–Co–N(33)	92.4(2)
		N(32)–Co–N(34)	90.1(2)
		N(33)–Co–N(34)	177.6(2)

(b) *The ligands (2-amt molecules)*

A = 1–4	A = 1	A = 2	A = 3	A = 4
S1A–C2A	1.741(4)	1.742(4)	1.731(4)	1.737(4)
C2A–N3A	1.301(5)	1.289(5)	1.315(5)	1.296(5)
N3A–C4A	1.390(5)	1.412(5)	1.395(4)	1.408(5)
C4A–C5A	1.323(5)	1.333(6)	1.344(5)	1.353(6)
C5A–S1A	1.720(4)	1.702(5)	1.730(4)	1.726(5)
C2A–N2A	1.361(6)	1.369(6)	1.354(5)	1.366(5)
C5A–S1A–C2A	88.8(2)	89.1(2)	89.5(2)	89.1(2)
S1A–C2A–N3A	114.4(3)	115.0(3)	114.6(3)	115.1(3)
C2A–N3A–C4A	109.9(3)	109.5(3)	109.8(3)	110.6(3)
N3A–C4A–C5A	116.4(3)	115.5(4)	116.2(3)	114.7(3)
C4A–C5A–S1A	110.4(3)	110.9(3)	109.8(3)	110.6(3)
N2A–C2A–S1A	122.3(3)	121.7(3)	121.3(3)	120.1(3)
N2A–C2A–N3A	123.2(4)	123.3(4)	124.1(3)	124.8(3)
C4A–N3A–Co	120.0(2)	118.1(2)	119.1(2)	120.3(3)
C2A–N3A–Co	129.3(3)	129.4(3)	129.3(2)	129.1(2)

(c) *Thiocyanate groups*

S(1)–C(1)	1.626(3)	S(2)–C(2)	1.625(4)
C(1)–N(1)	1.164(4)	C(2)–N(2)	1.149(5)
S(1)–C(1)–N(1)	177.9(3)	S(2)–C(2)–N(2)	178.6(4)
C(1)–N(1)–Co	158.5(3)	C(2)–N(2)–Co	161.8(3)

enthalpies, derived from the areas of these endotherms, are 84.7 and 145.0 kJ mol^{-1} respectively.

The combination of endotherm and exotherm is common for complexes of 2-*amt* and suggests that the presence of the metal catalyses the exothermic degradation of the ligand [13].

An X-ray study has shown the cobalt atom to be octahedrally coordinated by the heterocyclic nitrogen atoms of 2-*amt* and the nitrogen atoms of the thiocyanate groups, the latter have a *trans* disposition (Fig. 3). The discrete molecular complexes are held together largely by means of van der Waals' forces; there are no short intermolecular H-bonds (Fig. 4).

Angles around the cobalt atom (Table III) show the CoN$_6$ environment to be distorted. A similar conclusion may be derived from the mean planes data which show the cobalt atom to be significantly displaced from the mean planes of the heterocyclic molecules (Table IV). The 2-*amt* molecules are essentially planar but are significantly twisted out of the CoN$_4$ plane (Table IV, Fig. 3).

Bond lengths and angles within the 2-*amt* molecules are similar to those observed for free [5] and

TABLE IV. Equations of Selected Least-Squares Mean Planes with Atomic Displacements (A) and Relevant Dihedral Angles (°).

Plane 1	CoN_4 (Co N31 N32 N33 N34) $0.5861X + 0.3849Y + 0.7129Z - 2.9857 = 0.0$ [Co −0.033(10); N31 0.055(7); N32 0.053(8); N33 −0.037(8); N34 −0.038(9)]
Plane 2	Ligand 1 (S11 C21 N21 N31 C41 C51) $0.9746X - 0.2153Y + 0.0611Z + 0.3052 = 0.0$ [Co 0.347(1); S11 0.003(2); C21 0.005(8); N21 −0.001(6); N31 0.009(6); C41 −0.007(8); C51 0.001(8)]
Plane 3	Ligand 2 (S12 C22 N22 N32 C42 C52) $-0.0234X + 0.7406Y + 0.6715Z - 2.3311 = 0.0$ [Co 0.652(1); S12 0.017(2); C22 0.011(9); N22 −0.021(6); N32 0.018(7); C42 −0.006(9); C52 −0.019(7)]
Plane 4	Ligand 3 (S13 C23 N23 N33 C43 C53) $0.1668X + 0.9823Y + 0.0851Z - 1.1719 = 0.0$ [Co −0.537(1); S13 −0.010(2); C23 0.005(9); N23 0.008(6); N33 −0.019(10); C43 0.012(10); C53 0.004(10)]
Plane 5	Ligand 4 (S14 C24 N24 N34 C44 C54) $0.3769X - 0.4204Y + 0.8254Z - 3.2117 = 0.0$ [Co −0.024(1); S14 0.006(3); C42 0.012(10); N24 −0.014(6); N34 0.012(7); C44 −0.010(9); C54 −0.005(9)]

Planes	Dihedral Angle
1/2	57.9
1/3	41.4
1/4	57.6
1/5	49.6
2/3	81.8
4/5	63.8
2/4	87.5
3/4	38.7
2/5	59.4
3/5	76.5

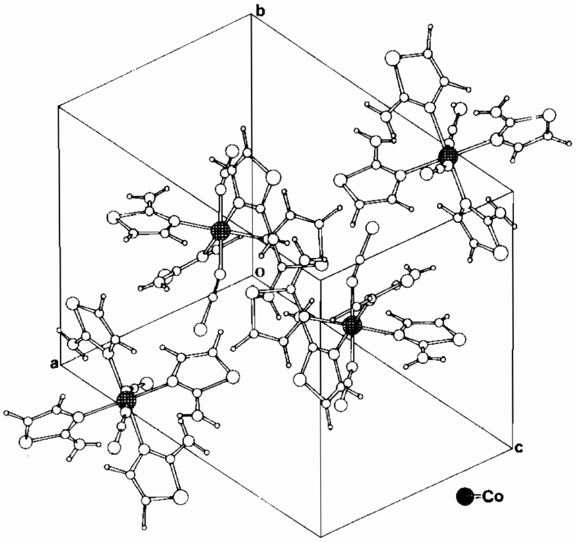

Fig. 4. Perspective view of the unit cell contents.

coordinated [6] amino-thiazoles. Significant localisation of π-density occurs within the N2A-C2A-N3A portion of the *2-amt* molecules. This suggests that the amino group is conjugated to the rest of the molecule.

Consequently the p_z electrons of the N2A atoms are involved in the π-MO scheme of the heterocyclic molecules and are not readily available for coordination. This leaves N3A, with its favourably orientated lone pair of electrons, as the preferred donor in *2-amt*. The resultant Co–N distances are similar to those reported for other CoN_6 heterocyclic systems [14, 15]. The Co–N(3)–C(2 & 4) angles are noticeably asymmetric (Table III) probably because of the steric effects of the amino groups. The thiocyanate group dimensions are normal.

The original proposal that *2-amt* is S-donating in $[Co(2\text{-amt})_4(NCS)_2]$ [4] is clearly erroneous, at least in the solid state. It is also likely that the heterocyclic nitrogen atom is the donor atom in the corresponding nickel and zinc complexes.

Acknowledgement

We are grateful to S.E.R.C. and Dr. M. B. Hursthouse, Department of Chemistry, Queen Mary

College, University of London, for the provision of X-ray intensity data.

References

1 A. K. Bayak and D. Banarjea, *J. Ind. Chem. Soc.*, *55*, 853 (1978).

2 P. P. Singh and A. K. Srivastava, *J. Inorg. Nucl. Chem.*, *36*, 928 (1974).

3 E. J. Duff, M. N. Hughes and K. J. Rutt, *Iorg. Chim. Acta*, *6*, 408 (1972).

4 P. P. Singh, V. P. Shukla and J. N. Seth, *Ind. J. Chem.*, *14A*, 684 (1976).

5 G. R. Form, E. S. Raper and T. C. Downie, *Acta Cryst.*, *B30*, 342 (1974).

6 E. S. Raper, R. E. Oughtred, I. W. Nowell and L. A. March, *Acta Cryst.*, *B37*, 928 (1981).

7 E. S. Raper, *J. Therm. Anal.*, *25*, 463 (1982).

8 'International Tables for X-ray Crystallography', (1974), Vol. IV, Table 2.2B, Birmingham, Kynoch Press.

9 G. M. Sheldrick, Programs for Crystal Structure Determination, Cambridge Univ., England (1976).

10 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, New York (1968).

11 E. Konig, 'Structure and Bonding', Vol. 9, pp. 175–212, Springer-Verlag, Berlin (1971).

12 R. J. H. Clarke and C. S. Williams, *Spectrochim. Acta*, *22*, 1081 (1966).

13 B. M. Jordan, E. S. Raper and J. R. Creighton, *Thermochim. Acta*, *62*, 21 (1983).

14 (a) H. Hartl and I. Brudgam, *Acta Cryst.*, *B36*, 162 (1980).
(b) H. Hartl and S. Steidl, *Acta Cryst.*, *B36*, 65 (1980).

15 (a) D. W. Engelfriet, W. Den Brinker, G. C. Verschoor and S. Gorter, *Acta Cryst.*, *B35*, 2922 (1975).
(b) D. W. Engelfriet, G. C. Verschoor and W. Den Brinker, *Acta Cryst.*, *B36*, 1554 (1980).

16 B. T. M. Willis and A. W. Pryor, 'Thermal Vibrations in Crystallography', Cambridge.