O(1) accepts two weak hydrogen bonds [H···O distances: 1·418 (1) and 1·877 (2) Å] from the water molecule.

That the C—C bond in C_2O_4 groups possesses some π character has been demonstrated experimentally and theoretically as peaks of deformation density in sections through the midpoint of the bond which are elongated normal to the C_2O_4 plane (Tellgren, Thomas & Olovsson, 1977; Stevens & Coppens, 1980, and references therein). However, in general the C_2O_4 group has an abnormally long sp^2–sp^2 single C—C bond which is lengthened stepwise as the acid molecule loses both protons (Küppers, 1973).

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Structure of Potassium Tetrakis(isothiocyanato)cobaltate(II) Monohydrate Nitromethane Solvate, K₂[Co(NCS)₄].H₂O.2CH₃NO₂, at 120 K by Neutron Diffraction

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Abstract. $M_r = 509·6$, monoclinic, $I2$ (conventional $C2$), $a = 11·098$ (2), $b = 5·227$ (1), $c = 16·496$ (3) Å, $\beta = 100·06$ (1)°, $V = 942·2$ (3) Å^3, $Z = 2$, $D_x = 1·796$, $D_m = 1·78$ g cm^{-3}, $\lambda = 1·0470$ (1) Å, $\mu = 0·771$ cm^{-1}, $T = 120$ K. Final $R(F^2) = 0·038$ for 2011 observed reflections. The structure is built from chains of approximately tetrahedral [Co(NCS)₄]²⁻ anions parallel to **b** and interconnected by O—H···S hydrogen bonds of length 3·377 (2) Å. The potassium ions are linked by the nitromethane and water molecules to give double chains also parallel to **b**. Average bond distances in the anion are Co—N 1·964 (2), N—C 1·173 (1) and C—S 1·627 (2) Å.

Introduction. As part of a program of study of the charge-density distributions in small coordination complexes, we have undertaken an analysis of the [Co(NCS)₄]²⁻ anion because of its well established electronic properties and the fact that detailed charge-density studies of the free thiocyanate ion have been carried out (Bats, Coppens & Kvick, 1977; Bats & Coppens, 1977). The structure of [Co(NCS)₄]²⁻ has been determined in combination with several different cations: Hg[Co(NCS)₄] (Jeffrey & Rose, 1968), K₂[Co(NCS)₄].3H₂O (Drew & Hamid bin Othman, 1975), Na₂[Co(NCS)₄].8H₂O (Mereiter & Preisinger, 1982) and [N(CH₃)₄]₂[Co(NCS)₄] (Hoffman & Wood,

1982); in the first three of these salts the tetrahedral anions pack together to form linear chains so that their structures are rather similar. However, the compounds listed above did not seem suitable for a charge-density analysis, either because the crystals belong to a non-centrosymmetric space group or because of problems associated with twinning. We therefore attempted to obtain suitable centrosymmetric crystals of the potassium salt by crystallization from different solvent mixtures. Although we were unsuccessful in this attempt, we found that use of a nitromethane/95% ethanol mixture gave excellent crystals, the room-temperature X-ray analysis of which showed an ordered structure with low thermal motion. We therefore decided to undertake a detailed analysis of this salt, which in fact turned out to be a nitromethane solvate with a structure very closely related to that of the trihydrate, $K_2[Co(NCS)_4].3H_2O$ (Drew & Hamid bin Othman, 1975). The present paper reports the details of the neutron structure analysis carried out in conjunction with the charge-density study, for which the X-ray data were collected at 117 (5) K.

Experimental. The tetrathiocyanate complex was prepared from $Co(NO_3)_2.6H_2O$ and KSCN and the title compound crystallized from a nitromethane–ethanol solution of the complex. Diffractometer used: four-circle instrument; Brookhaven High Flux Beam Reactor; monochromator: Be crystal, 002 reflection; $34.2°$ take-off angle. Cryostat: DISPLEX®Model CS-202 (Air Products and Chemicals, Inc.). Cell dimensions: from 32 reflections in range $40 \leq 2\theta \leq 57°$. Crystal dimensions: $3.52 \times 1.20 \times 1.38$ mm bounded by {010}, {101}, {10$\bar{1}$} and {001}, volume 4·28 mm³, weight 7·45 mg. Density measured by flotation at 295 K. Absorption corrections: Gaussian integration; min. and max. transmission factors, 0·896 and 0·929. Intensity measurements: $\omega/2\theta$ step-scan; quadrant $(-h\ k\ \pm l)$; $\sin\theta/\lambda \leq 0.78$ Å⁻¹. Reflections recorded: 2108 total, 2047 independent; internal agreement for zonal reflections $R = 0.026$. Total of 2047 independent reflections $(h\ -17\rightarrow0,\ k\ 0\rightarrow7,\ l\ -24\rightarrow25)$ measured in range $4 \leq 2\theta \leq 110°$ using ω–2θ step scans. Two standards measured every 50 reflections – no significant variation in intensity with time. Step scans analyzed using *PROFILE* (Blessing, Coppens & Becker, 1974). Standard deviations assigned as $\sigma(I) = [\sigma_c^2(I) + (0.014I)^2]^{1/2}$ where $\sigma_c(I)$ is based on counting statistics. Initial coordinates for all atoms taken from room-temperature X-ray analysis (Hoffman & Wood, 1981, unpublished work). Least-squares refinement: function minimized $\sum w(F_o^2 - F_c^2)^2$ with weights $w = [\sigma(I)\sin2\theta]^{-1}$. Observations used: 2011 reflections with $I > 0$. Computer program: *LINEX*74, a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Refinement of 146 variables included positional and anisotropic thermal parameters, scale factor and an isotropic extinction parameter for type I crystal with Lorentzian distribution of mosaicity (Becker & Coppens, 1974). Largest extinction correction, $1.08\ F_o^2$. $R(F^2) = 0.038$, $R_w(F^2) = 0.029$ and $S = 1.32$ at convergence with all $\Delta p_i \leq 0.08\sigma(p_i)$. Max. value in final difference map: 1·3% peak height for nitrogen. Neutron scattering lengths: Koester (1977). Calculations carried out on CDC-Cyber 175 computer. In penultimate cycles the cobalt scattering length was refined and this converged to a value of 2·33 (2) fm, compared to 2·48 (2) fm reported for the Co atom in $Co_3(CO)_4CH$ (Leung, Coppens, McMullan & Koetzle, 1981) and to the two literature values (Koester, 1977) of 2·78 (4) and 2·50 (5) fm. Although smaller than previously refined values, in view of probable error accumulation at the origin and the discrepancy between the literature values we do not attach significance to the difference.

Discussion. Final atomic parameters are listed in Table 1.* The structure of $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$, illustrated by means of two *ORTEP* projections (Johnson, 1965) in Figs. 1 and 2, is built up of tetrahedral $[Co(NCS)_4]^{2-}$ anions packed efficiently into chains parallel to the crystal b axis. These chains are interconnected in the **a** direction through O—H⋯S hydrogen bonds between two of the (translation-related) thiocyanate ligands and the water molecule (Fig. 1). The O⋯S distance of 3·377 (2) Å is in accord with recently tabulated values for this interaction (Mereiter, Preisinger & Guth, 1979). The water and nitromethane molecules, together with the potassium ions, form a ladder-like chain arrangement parallel to **b**, the repeat unit of the chain being [H₂O.K₂(CH₃NO₂)₂]. Four oxygen atoms, three of nitromethane and one of water, together with three sulfur atoms at an average distance of 3·349 (2) Å form an irregular coordination sphere about the potassium ion. The nitromethane molecule can be viewed as being essentially bidentate towards the potassium ion, the two pertinent K⁺⋯O distances being 2·925 (2) and 3·110 (2) Å, while oxygen O(2) also bridges the translation-related K⁺ ions.

There is a close relationship between the present structure and that of the trihydrate salt $K_2[Co(NCS)_4].3H_2O$ (Drew & Hamid bin Othman, 1975), for while the nitromethane molecules replace the water molecules in general positions in the latter structure, the form of the double cation chains and their role in linking the anion chains remain the same. The principal difference between the two structures is that for the trihydrate, the tetrahedra in one half of the anion

Table 1. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *for* $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$

	x	y	z	U_{eq}†
K	34199 (15)	3708 (37)	10741 (9)	167 (6)
Co	0	0	0	123 (15)
N(1)	7009 (6)	22758 (18)	9078 (4)	191 (3)
N(2)	−13049 (6)	−22032 (18)	2735 (4)	179 (3)
C(1)	10811 (8)	39844 (22)	13394 (5)	137 (3)
C(2)	−19748 (7)	−38012 (23)	4199 (5)	140 (3)
S(1)	16402 (19)	63414 (47)	19321 (11)	163 (8)
S(2)	−29373 (19)	−59644 (48)	6178 (13)	181 (9)
C(3)	62068 (9)	45033 (24)	27164 (6)	199 (4)
N(3)	54330 (6)	61111 (20)	20882 (4)	161 (3)
O(1)	56701 (11)	83920 (28)	20661 (8)	259 (6)
O(2)	46031 (10)	51046 (29)	16098 (7)	224 (5)
H(1)	64966 (34)	56554 (72)	32474 (16)	619 (18)
H(2)	56827 (31)	29037 (75)	28516 (24)	701 (19)
H(3)	69868 (30)	39711 (94)	24567 (22)	728 (23)
O(3)	$\frac{1}{2}$	86994 (38)	0	207 (7)
H(4)	44513 (24)	75278 (66)	−3269 (16)	455 (14)

† $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i.\mathbf{a}_j a_i^* a_j^*$.
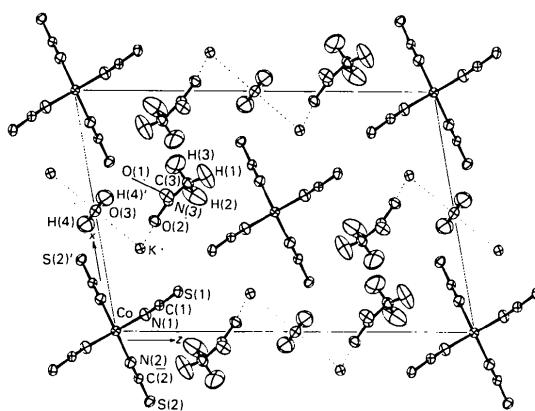
Fig. 1. The structure of $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$ in (010) projection. Thermal ellipsoids are at the 67% probability level. Hydrogen bonds are dotted and the $K^+\cdots O$ interactions indicated by broken lines.
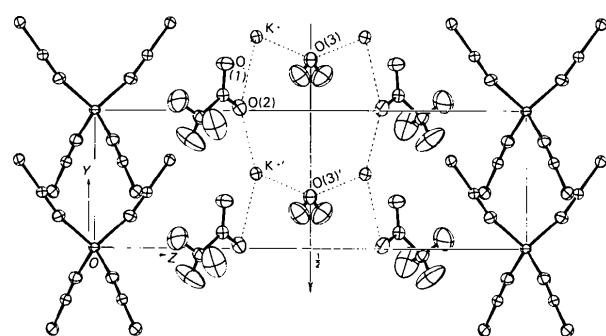

Fig. 2. A portion of the structure of $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$ projected onto (100) and showing the double cation chains.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$

(i) The $[Co(NCS)_4]^{2-}$ ion

Co−N(1)	1·964 (2)	Co−N(2)	1·963 (2)
N(1)−C(1)	1·174 (1)	N(2)−C(2)	1·171 (1)
C(1)−S(1)	1·627 (2)	C(2)−S(2)	1·627 (2)
Co−N(1)−C(1)	167·5 (1)	Co−N(2)−C(2)	170·7 (1)
N(1)−C(1)−S(1)	178·6 (1)	N(2)−C(2)−S(2)	178·4 (1)
N(1)−Co−N(1)'	105·4 (2)ª	N(2)−Co−N(2)'	108·1 (2)
N(1)−Co−N(2)	113·0 (2)	N(2)−Co−N(1)'	108·7 (2)

(ii) The CH_3NO_2 molecule

O(1)−N(3)	1·221 (1)	O(2)−N(3)	1·222 (1)
C(3)−N(3)	1·486 (1)	C(3)−H(1)	1·065 (3)
C(3)−H(2)	1·064 (3)	C(3)−H(3)	1·068 (3)
O(1)−N(3)−O(2)	122·8 (1)	N(3)−C(3)−H(1)	108·0 (2)
O(1)−N(3)−C(3)	118·1 (1)	N(3)−C(3)−H(2)	108·7 (2)
O(2)−N(3)−C(3)	119·0 (1)	N(3)−C(3)−H(3)	106·1 (2)
H(1)−C(3)−H(2)	111·7 (3)	H(2)−C(3)−H(3)	113·0 (4)
H(1)−C(3)−H(3)	109·1 (3)		

(iii) The water molecule

H(4)−O(3)	0·960 (3)	H(4)−O(3)−H(4)'	100·7 (4)

(iv) Selected intermolecular parameters

O(3)⋯S(2)'	3·377 (2)	O(3)⋯K⁺	2·839 (2)
H(4)⋯S(2)'	2·470 (3)	O(2)⋯K⁺	2·867 (2)
O(3)−H(4)⋯S(2)'	157·4 (4)	O(1)ᵇ⋯K⁺	2·925 (2)
		O(2)ᵇ⋯K⁺	3·110 (2)

(a) A prime represents a twofold-related atom.
(b) Atoms at $x, y−1, z$.

chains have a reverse orientation with respect to those in the nitromethane adduct, which all have the same orientation. Interatomic distances and angles, uncorrected for librational motion, are listed in Table 2. The water molecule bond angle of 100·7 (4)° is appreciably smaller than the gas-phase value of 104·5° and the average of 107° listed in a recent survey of hydrogen-bond parameters involving water (Chiari & Ferraris, 1982). For nitromethane, the chemically equivalent bond lengths are equal in length within 1σ, and its conformation is similar to that of acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980) with the heavy atoms being virtually coplanar and the C−H bonds being normal to the plane within a few degrees.

There are appreciable angular distortions of the CoN_4 coordination polyhedron from T_d symmetry and also of the whole anion from D_{2d} symmetry, which, allowing for the departure of the Co−N−C angles from linearity, is the highest point-group symmetry attainable. Thus the dihedral angle between the planes intersecting in the C_2 axis and defined by the Co and the pairs of twofold-related nitrogen atoms is 86·5 (2)° while the angles bisected by the twofold axis are 105·4 (2) and 108·1 (2)°. These angular distortions appear to be attributable to the differing intermolecular interactions between the anions and the three other species in the cell. The Co−N distances and the

distances and angles within the thiocyanate groups obtained from this neutron study are closely in accord with those reported for room-temperature analyses (*e.g.* Mereiter & Preisinger, 1982).

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Struktur von Triethylammonium Pentacarbonyl(diphenylphosphinito-*P*)wolfram(0), [NH(C₂H₅)₃][W(C₁₂H₁₀OP)(CO)₅]

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Abstract. $M_r = 627\cdot29$, triclinic, $P\bar{1}$, $a = 10\cdot795$ (2), $b = 10\cdot828$ (3), $c = 12\cdot131$ (3) Å, $\alpha = 114\cdot95$ (3), $\beta = 95\cdot85$ (3), $\gamma = 94\cdot99$ (3)°, $V = 1265\cdot5$ Å³, $Z = 2$, $D_x = 1\cdot646$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 47\cdot582$ cm⁻¹, $F(000) = 616$, $T = 293$ K; refinement converged to $R = 0\cdot023$, $R_w = 0\cdot026$ [4441 reflections with $I > 3\sigma(I)$]. The W atom was found to have a nearly octahedral coordination formed by the diphenylphosphinito-*P* and five carbonyl ligands, and the P atom a distorted tetrahedral coordination of two phenyl groups, one O and one W atom. The very short N···O distance of 2·603 (5) Å and the N–H = 0·95 (4) Å and H···O = 1·66 (4) Å distances (H position from least-squares refinement) indicate the existence of a very strong N–H···O hydrogen bond between the ammonium and the phosphinite group.

Einleitung. Diorganylphosphinigsäuren und -phosphinite R_2PX ($X = $ OH, OR', O⁻) sind mit Ausnahme der perfluorierten Derivate im freien Zustand unbekannt (Griffiths & Burg, 1960, 1962). Sie lassen sich jedoch als Liganden an Übergangsmetall-Komplexen gezielt aufbauen und stabilisieren (Roundhill, Sperline & Beaulieu, 1978). Kraihanzel & Bartish (1972) beschreiben die Syntheses von [(C₂H₅)₃NH][O(C₆H₅)₂PMo(CO)₅] durch Hydrolyse von (CO)₅MoP(C₆H₅)₂Cl mit Triethylamin. Wir können dieses Ergebnis bestätigen und auf die anderen 6*A*-Elementhomologen erweitern (Zeiher, 1984). Geeignete Einkristalle dieser Salze erhielten wir jedoch bei der basischen Hydrolyse der entsprechenden Diphosphoxan-Komplexe [(CO)₅*M*P(C₆H₅)₂]₂O (*M* = Cr, Mo, W) (Zeiher, Mohyla, Lorenz & Hiller, 1984). Zur eindeutigen Charakterisierung dieser isotypen Diphenylphosphinito-*P*-Komplexe und zur Klärung der Frage nach möglichen Wasserstoff-Brückenbindungen N–H···O zwischen beiden ionischen Molekülteilen wurde stellvertretend an der Wolframverbindung eine Kristallstrukturbestimmung durchgeführt.

Experimentelles. Schwach gelbliche, stäbchenförmige Kristalle durch mehrtägige Kristallisation aus Diethyl-