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## SHORT STRUCTURAL PAPERS

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### Pentapotassium Pentasodium Bis[*cis*-tetracyanodisulphitocobaltate(III)] Enneahydrate

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**Abstract.**  $\text{K}_5\text{Na}_5[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2]_2 \cdot 9\text{H}_2\text{O}$ ,  $M_r = 1118.8$ , triclinic,  $P\bar{1}$ ,  $a = 8.057$  (3),  $b = 9.253$  (3),  $c = 12.817$  (2) Å,  $\alpha = 104.01$  (2),  $\beta = 98.77$  (2),  $\gamma = 96.39$  (3)°,  $Z = 1$ ,  $D_m = 2.00$  (5),  $D_c = 2.05$  Mg m $^{-3}$ ,  $\mu(\text{Mo } K\alpha) = 1.89$  mm $^{-1}$ . Least-squares refinement (3285 reflections, single-crystal X-ray diffractometer data) gave  $R = 0.044$  for 259 parameters. The configuration of ligands about Co is approximately octahedral with the sulphite groups *cis* and mean Co–S = 2.262 (1), S–O = 1.473 (2), Co–C = 1.891 (2) and C–N = 1.156 (2) Å. There is no evidence for a sulphite *trans* effect. Three of the  $\text{K}^+$  ions and the O atom of one water molecule occupy their sites statistically and have been assigned occupancy 0.5.

**Introduction.** In connection with structural studies of transition-metal cyano complexes the mode of coordination of sulphite in the presence of cyanide and its effect on the metal  $\rightarrow \pi^*(\text{CN})$  transfer is of interest. In  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{SO}_3] \cdot 10\frac{1}{2}\text{H}_2\text{O}$  (Jagner, Ljungström & Tullberg, 1980), in which  $-\text{SO}_3$  is bonded to Fe through S, the Fe–S and S–O distances suggested the presence of Fe–S  $d_\pi-d_\pi$  bonding. In order to investigate this point further, the crystal structures of some cyanosulphitocobaltates are being investigated, that of  $\text{K}_5\text{Na}_5[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2]_2 \cdot 9\text{H}_2\text{O}$  being reported here.

Yellow plates of the title compound were prepared from  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ ,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  and KCN, according to the method of Siebert, Siebert & Thym (1971) for  $\text{K}_3\text{Na}_2[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . The present formulation of the compound is in accordance with its crystal structure. The K:Na:Co molar ratio, 2.6:2.5:1.0, was confirmed by atomic-absorption spectroscopy, using a Perkin–Elmer 403 spectrometer and a sample of single crystals picked out under the microscope. The error associated with the determination of these metals by atomic-absorption spectroscopy is of the order of  $\pm 2\%$ . The density was measured by flotation in  $\text{CHCl}_3/\text{CHBr}_3$ .

Intensities from a crystal,  $0.19 \times 0.18 \times 0.09$  mm, were measured at 168 K with a Syntex  $P2_1$  diffractometer, using graphite-monochromatized Mo  $K\alpha$  radiation and the  $\omega-2\theta$  scan technique, with a variable scan rate of 2–8° min $^{-1}$  in  $2\theta$ . Data were collected for  $\sin \theta/\lambda \leq 0.617$  Å $^{-1}$  with  $h \geq 0$ , 3842 reflections being measured. That the crystal was not subject to decay was verified by the periodical measurement of the intensities of two reflections. A 96-step profile was recorded for each reflection and the Lehmann & Larsen (1974) method was used to calculate the intensities (Lindqvist & Ljungström, 1979). Correction was made for Lorentz and polarization effects but not for absorption or extinction. Symmetry-related reflections were averaged

giving 3573 unique reflections. Of these 3285 for which  $I > 3.0\sigma(I)$  were used in the subsequent calculations. The unit-cell parameters at 168 K and their standard deviations were determined by least squares from diffractometer setting angles for 15 reflections.

The structure was solved from Patterson and successive electron density maps. From block-diagonal least-squares refinement of positional and isotropic thermal parameters it was apparent that K(1) and Aq(5)\* did not lie exactly in  $\frac{1}{2}0\frac{1}{2}$  and  $\frac{1}{2}10$  respectively. Moreover, it was not possible to assign a K<sup>+</sup> ion wholly to one of the sites K(3) or K(4), an occupancy of 0.5 in each yielding the most satisfactory agreement ( $R = 0.094$ ). Attempts were made to refine the structural parameters in  $P1$ , both chemically reasonable combinations of the disordered atoms being tested. Neither of these models, however, refined under  $R = 0.11$ , unreasonable interatomic distances within the two complex ions and large discrepancies between lengths of comparable bonds being obtained in both cases. Since, moreover, statistical tests (*MULTAN*, Main,

Woolfson, Germain & Declercq, 1977) indicated the presence of a centre of symmetry, the final refinement of the structure was based on the partially disordered model in  $P\bar{1}$ .

Block-diagonal least-squares refinement of the positional and anisotropic thermal parameters and a scale factor yielded  $R = 0.044$  for 259 parameters (3285 reflections); when the 288 unobserved reflections were included  $R = 0.048$ . The  $F_o$  values were weighted according to  $w = (a + F_o + cF_o^2)^{-1}$  (Cruickshank, 1970) with  $a = 40.0$  and  $c = 0.005$ . Scattering factors for Co, C, N, S, O, Na and K were taken from Doyle & Turner (1968). No attempt was made to refine the occupation factors of the disordered atoms. A final difference map showed a maximum electron density of  $1.1 \text{ e } \text{Å}^{-3}$ . H atoms were not located. Atomic coordinates are listed in Table 1.\* Calculations were carried out on an IBM 360/65-370/145 computer system using programs described by Lindgren (1977); drawings were prepared with *ORTEP* (Johnson, 1965).

\* Aq denotes the O atom of a water molecule.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{Å}^2$ ) with e.s.d.'s in parentheses

$$B_{\text{eq}} = 8\pi^2/3 (U_{11} a^{*2} a^2 + \dots + U_{23} b^* c^* bc \cos \alpha),$$

the anisotropic temperature factor being defined as:

$$T = \exp [-2\pi^2 (U_{11} h^2 a^{*2} + \dots + U_{23} klb^* c^*)].$$

Disordered atoms with occupancy 0.5 are marked with an asterisk.

	x	y	z	$B_{\text{eq}}$
Co	0.24319 (6)	0.27717 (5)	0.26775 (4)	0.78 (1)
S(1)	0.00398 (11)	0.34267 (10)	0.18719 (8)	0.99 (1)
O(11)	-0.0819 (4)	0.2228 (4)	0.0882 (3)	2.42 (6)
O(12)	-0.1183 (4)	0.3698 (4)	0.2620 (2)	2.20 (6)
O(13)	0.0452 (4)	0.4814 (4)	0.1522 (4)	4.00 (8)
S(2)	0.09813 (11)	0.05896 (9)	0.27905 (7)	0.88 (1)
O(21)	0.2142 (4)	-0.0239 (4)	0.3328 (4)	3.76 (7)
O(22)	-0.0345 (4)	0.0879 (4)	0.3450 (4)	4.52 (8)
O(23)	0.0161 (7)	-0.0400 (4)	0.1720 (3)	5.40 (9)
C(1)	0.2926 (5)	0.1835 (4)	0.1299 (3)	1.31 (6)
N(1)	0.3284 (5)	0.1259 (4)	0.0474 (3)	2.13 (7)
C(2)	0.2093 (5)	0.3744 (4)	0.4084 (3)	1.10 (6)
N(2)	0.1899 (4)	0.4323 (4)	0.4951 (3)	1.38 (6)
C(3)	0.4487 (5)	0.2298 (4)	0.3355 (3)	1.30 (6)
N(3)	0.5766 (4)	0.2042 (4)	0.3747 (3)	1.90 (6)
C(4)	0.3749 (5)	0.4577 (4)	0.2644 (3)	1.51 (7)
N(4)	0.4627 (5)	0.5659 (4)	0.2641 (3)	2.35 (7)
Na(1)	0	0	0	1.23 (4)
Na(2)	-0.1291 (2)	0.3105 (2)	0.4335 (1)	1.35 (3)
Na(3)	0.7838 (2)	0.6172 (2)	0.3206 (1)	1.61 (3)
K(1)*	0.4737 (3)	-0.0248 (3)	0.4861 (2)	2.65 (5)
K(2)	0.66268 (11)	0.06632 (11)	0.16190 (8)	1.80 (2)
K(3)*	0.2519 (3)	0.5842 (2)	0.0217 (2)	2.73 (4)
K(4)*	0.1906 (3)	0.6752 (2)	0.0758 (2)	2.51 (4)
Aq(1)	0.7731 (4)	0.8780 (3)	0.4201 (3)	1.94 (5)
Aq(2)	0.8034 (6)	0.6929 (4)	0.1543 (3)	4.51 (9)
Aq(3)	0.4488 (5)	0.8471 (4)	0.2057 (5)	4.78 (10)
Aq(4)	0.1024 (4)	0.7158 (3)	0.3852 (3)	2.01 (5)
Aq(5)*	0.4264 (10)	0.4751 (10)	0.0110 (7)	3.84 (16)

**Discussion.** Bond lengths and angles within the [*cis*-Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>5-</sup> ion are given in Table 2 and a perspective view of the ion is shown in Fig. 1. Both sulphite ligands are coordinated to Co through S, the mean Co—S, 2.262 (1) Å, and S—O, 1.473 (2) Å [mean

\* Lists of structure factors, anisotropic thermal parameters, and O...O and O...N contacts <3 Å and a stereoview of the unit cell have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36277 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) within the [Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>5-</sup> ion

Co—S(1)	2.259 (1)	Co—S(2)	2.265 (1)
Co—C(1)	1.892 (4)	Co—C(3)	1.896 (4)
Co—C(2)	1.885 (4)	Co—C(4)	1.890 (4)
S(1)—O(11)	1.483 (4)	S(2)—O(21)	1.468 (4)
S(1)—O(12)	1.476 (3)	S(2)—O(22)	1.469 (4)
S(1)—O(13)	1.479 (4)	S(2)—O(23)	1.462 (4)
C(1)—N(1)	1.157 (5)	C(3)—N(3)	1.151 (5)
C(2)—N(2)	1.153 (5)	C(4)—N(4)	1.161 (5)
Co—C(1)—N(1)	177.6 (4)	Co—C(3)—N(3)	177.5 (3)
Co—C(2)—N(2)	178.9 (3)	Co—C(4)—N(4)	176.7 (4)
Co—S(1)—O(11)	111.1 (1)	Co—S(2)—O(21)	109.9 (1)
Co—S(1)—O(12)	111.6 (1)	Co—S(2)—O(22)	111.2 (2)
Co—S(1)—O(13)	110.3 (1)	Co—S(2)—O(23)	112.8 (2)
O(11)—S(1)—O(12)	107.8 (2)	O(21)—S(2)—O(22)	107.2 (2)
O(11)—S(1)—O(13)	107.3 (2)	O(21)—S(2)—O(23)	107.9 (2)
O(12)—S(1)—O(13)	108.4 (2)	O(22)—S(2)—O(23)	107.6 (3)
S(1)—Co—C(1)	91.3 (1)	S(2)—Co—C(1)	92.0 (1)
S(1)—Co—C(2)	91.8 (1)	S(2)—Co—C(2)	90.0 (1)
S(1)—Co—C(3)	177.7 (1)	S(2)—Co—C(3)	90.7 (1)
S(1)—Co—C(4)	91.7 (1)	S(2)—Co—C(4)	176.6 (1)
S(1)—Co—S(2)	91.6 (1)	C(2)—Co—C(3)	88.0 (2)
C(1)—Co—C(2)	176.3 (2)	C(2)—Co—C(4)	88.9 (2)
C(1)—Co—C(3)	88.8 (2)	C(3)—Co—C(4)	86.1 (2)
C(1)—Co—C(4)	88.8 (2)		

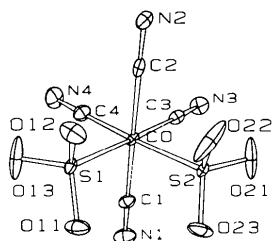


Fig. 1. Perspective view of the [*cis*-Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>5-</sup> ion.

of six distances], lying within the range of values reported for sulphite complexes of Co<sup>III</sup> (Fallon, Raston, White & Yandell, 1980). The Co<sup>III</sup>—S distances in [*cis*-Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>5-</sup> are very similar to the Fe<sup>II</sup>—S distances [2.255 (1), 2.277 (1) Å] in [Fe(CN)<sub>5</sub>SO<sub>3</sub>]<sup>5-</sup> (Jagner *et al.*, 1980). Assuming  $\sigma$  bonding only, Co<sup>III</sup>—S would be expected to be of the order of 0.1 Å shorter than Fe<sup>II</sup>—S [see *e.g.* the effective ionic radii of Shannon & Prewitt (1969)]. That these bond lengths are, in fact, closely similar would appear to support the suggestion that there is an appreciable  $d_{\pi}$ — $d_{\pi}$  contribution to the Fe—S bond in [Fe(CN)<sub>5</sub>SO<sub>3</sub>]<sup>5-</sup>. This is also borne out by the S—O distances in the two complex ions, *viz* mean S—O of 1.473 (2) Å in [*cis*-Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>5-</sup> as compared with 1.505 (1) Å in [Fe(CN)<sub>5</sub>SO<sub>3</sub>]<sup>5-</sup>.

The complex ion has approximately *mm*2 (*C*<sub>2v</sub>) symmetry. There appears, however, to be a trend towards slightly longer S—O [mean 1.479 (2) Å] accompanying a slightly shorter Co—S, 2.259 (1) Å, for ligand (1) and *vice versa* for ligand (2) [mean S—O 1.466 (2); Co—S(2) 2.265 (1) Å]. This is undoubtedly due to differences in the environment of the O atoms of the sulphite groups. The mean non-bonded O...O contacts<sup>†</sup> are 2.392 (2) Å for sulphite (1) and 2.366 (3) Å for sulphite (2). The closest distances of approach between the two groups are O(11)...O(23) 3.021 (5) and O(12)...O(22) 3.148 (5) Å.

The mean Co—C and C—N distances, 1.891 (2) and 1.156 (2) Å respectively, do not differ from those determined for [Co(CN)<sub>6</sub>]<sup>3-</sup>, *e.g.* in K<sub>3</sub>[Co(CN)<sub>6</sub>] (Vannerberg, 1972) and in Cs<sub>2</sub>Li[Co(CN)<sub>6</sub>] (Swanson & Ryan, 1973). This suggests a moderate Co →  $\pi^*$ (CN) transfer, comparable to that in [Co(CN)<sub>6</sub>]<sup>3-</sup> (Vannerberg, 1972, 1976). As is seen from Table 2, there is no evidence for a sulphite *trans* effect such as is usually found in Co<sup>III</sup> sulphite complexes with a  $\sigma$  donor, incapable of  $\pi^*$  acceptance, *trans* to sulphite (Raston, White & Yandell, 1980, and references therein). A similar situation was found in [Fe(CN)<sub>5</sub>SO<sub>3</sub>]<sup>5-</sup>, cyanide  $\sigma$  donation and metal →  $\pi^*$ (CN) transfer, even if only moderate as in the Co complex, apparently being sufficient to negate the normal *trans* influence of —SO<sub>3</sub>.

<sup>†</sup> See deposition footnote.

The Na<sup>+</sup>...O and Na<sup>+</sup>...N contacts range from 2.309 (4)—2.685 (4) Å. K(2) has eight O or N contacts in the range 2.733 (4)—3.108 (4) Å, and the disordered K(1), K(3) and K(4) ions have O or N contacts in the ranges 2.644 (5)—3.062 (5), 2.781 (8)—3.036 (5) and 2.506 (4)—3.197 (5) Å respectively. Some of these distances are rather short for K<sup>+</sup>...N or K<sup>+</sup>...O, and data collected from a crystal taken from a batch prepared prior to that described here (*R* = 0.089, 2545 reflections, isotropic thermal parameters) indicated that the K(3) and K(4) sites, in addition to being partially occupied, contained both Na<sup>+</sup> and K<sup>+</sup>, a mean scattering-factor curve for K and Na being employed. This would correspond to the formula K<sub>4</sub>Na<sub>6</sub>[Co(CN)<sub>4</sub>(SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·9H<sub>2</sub>O. Unfortunately, it was not possible to pick out a sufficiently large number of crystals from this batch to permit chemical analysis. These results appear to indicate that varying amounts of K<sup>+</sup> and Na<sup>+</sup> might be incorporated in the compound without changing its crystal structure. This has not, however, been investigated further. Since both structural and chemical analyses were in agreement for the batch from which the present crystal was taken, no attempt was made to introduce Na<sup>+</sup> into the K(1), K(3) or K(4) sites.

The disorder might be explained in terms of equal occurrence of both the chemically feasible arrangements of the disordered atoms in *P*1, *i.e.* in terms of twinning on either a macro or a micro scale. There was, however, no visible evidence of twinning or of OD behaviour (Dornberger-Schiff, 1966). The pronounced anisotropy of the thermal ellipsoids of O(13), O(21) and O(22) suggests that these atoms may perhaps also be involved in the disorder. Both O(21) and O(13) exhibit short contacts to K(4), whereas O(22), on the other hand, has contacts to ordered atoms only.

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## Structure de l'Hexachlorure de Cadmium et de Dinickel Dodécahydraté

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**Abstract.** CdNi<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O, *P*3,  $a = b = 9.9509$  (7),  $c = 11.2393$  (7) Å,  $D_m = 2.23$  (3) Mg m<sup>-3</sup>,  $Z = 2$ ,  $\mu(\text{Mo } K\alpha) = 3.808$  mm<sup>-1</sup>;  $R = 0.035$ ,  $R_w = 0.041$  for 3852 reflections. Each Cd atom is bonded to six Cl atoms and each Ni atom is bonded to six H<sub>2</sub>O molecules. The structure consists of stoichiometric layers of CdCl<sub>6</sub> and Ni(H<sub>2</sub>O)<sub>6</sub>. All the octahedra are linked together by hydrogen bonds.

**Introduction.** Dans le diagramme ternaire CdCl<sub>2</sub>–NiCl<sub>2</sub>–H<sub>2</sub>O, Bassett, Henshall, Sergeant & Shipley (1939) mirent en évidence des sels doubles de formule générale Cd<sub>x</sub>Ni<sub>y</sub>Cl<sub>2(x+y)</sub>·zH<sub>2</sub>O. De tels composés permettent de comparer le comportement structural de chacun des deux cations en présence de l'autre.

Après avoir étudié les hydrates Cd<sub>2</sub>NiCl<sub>6</sub>·12H<sub>2</sub>O (Leclaire & Borel, 1980*a*) et Cd<sub>4</sub>NiCl<sub>10</sub>·10H<sub>2</sub>O (Leclaire & Borel, 1980*b*), nous avons entrepris la détermination de la structure du composé CdNi<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O.

Les cristaux obtenus sont de couleur verte et souvent maclés. Ils se présentent sous des aspects divers, tels que des prismes aplatis, des étoiles ou des aiguilles. Les monocristaux utilisés au cours de cette étude étaient des aiguilles de section triangulaire.

Les dosages du cadmium, du nickel et du chlore sont en accord avec la formule pondérale CdNi<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O.

Les symétries observées sur les clichés réalisés à l'aide d'une chambre de Buerger sont compatibles avec

les groupes spatiaux *P*3 et *P*3̄. La structure n'a pu être résolue et affinée que dans le groupe *P*3. Les paramètres de la maille ont été obtenus à partir de coordonnées angulaires de 25 réflexions soigneusement centrées sur la diffractomètre.

L'enregistrement du spectre de diffraction d'un cristal en forme de prisme triangulaire de 0,32 mm de côté et 0,60 mm de hauteur, scellé dans un tube capillaire en verre de Lindemann contenant de l'huile de paraffine, a été réalisé sur un diffractomètre CAD-4 Enraf–Nonius avec le rayonnement *K* $\alpha$  du molybdène ( $\lambda = 0,71069$  Å) isolé par un monochromateur à lame de graphite. Les mesures ont été faites jusqu'à  $\theta = 45^\circ$  avec un balayage  $\omega - 2\theta$  d'amplitude  $(1,05 + 0,35 \text{ tg } \theta)^\circ$  et une ouverture de compteur de  $(3,00 + 0,80 \text{ tg } \theta)$  mm. Les réflexions ayant un  $\sigma(I)/I > 0,018$  ont été mesurées à nouveau avec une vitesse de balayage ajustée, de façon à avoir ou à approcher  $\sigma(I)/I < 0,018$  pour un temps de mesure limité à 60 s. Le fond continu a été déterminé en étendant l'intervalle de balayage de 25% de part et d'autre de la réflexion. La mesure de trois réflexions de contrôle toutes les 6000 s a montré que le cristal utilisé n'était pas altéré par le rayonnement X. Les mesures ont été corrigées des phénomènes de Lorentz, de polarisation et enfin de l'absorption à l'aide du programme *AGNOSTC* (Coppens, Leiserowitz & Rabinovich, 1965; de Meulenaer & Tompa, 1965).

3852 réflexions indépendantes répondant au critère *I*