Synthesis and Crystal Structure of the Hexakis(thiocyanato-*N*)-cobaltate(II) Anion†

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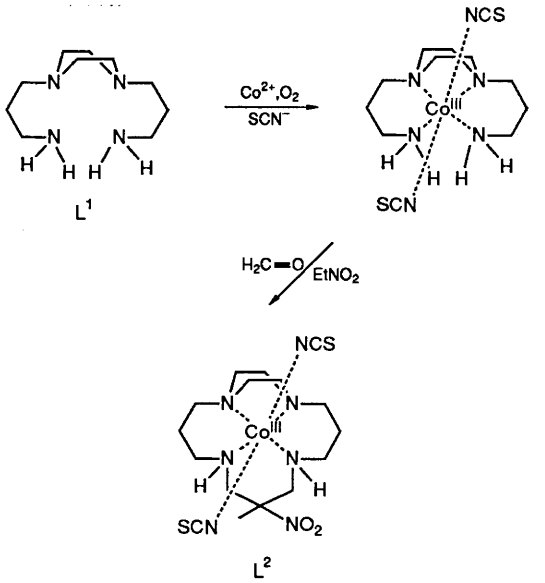
The synthesis and structure of $[H_4L^1][Co(NCS)_6]$ is described in which the cation is the tetra-protonated form of the tetraamine *N,N'*-bis(3-aminopropyl)piperazine(L^1). The pale red crystals are monoclinic, space group $P2_1/c$ (no. 14), with $a = 7.215(1)$, $b = 8.815(1)$, $c = 21.270(2)$ Å, $\beta = 91.82(1)°$ and $Z = 2$. The final conventional R factor was 0.0372. Cobalt(II) in the $[Co(NCS)_6]^{4-}$ ion is co-ordinated octahedrally with an average Co–N bond length of 2.11 Å.

Of the transition metals the Co^{II} ion forms tetrahedral complexes most readily,[1] and the tetrahedral $[Co(NCS)_4]^{2-}$ ion typifies this tendency. A search of the literature indicates that only the dark blue tetrahedral $[Co(NCS)_4]^{2-}$ ion is known, except for a report of the use of $[Co(NCS)_6]^{4-}$ salts in a Patent. There is also an example of Co^{II} in an octahedral environment of thiocyanates in a complex with mercury where bridging thiocyanate groups are present, *S*-bonded to Hg and *N*-bonded to Co^{II}.[2] We were thus surprised to isolate what appeared to be the $[Co(NCS)_6]^{4-}$ anion during synthetic work aimed at a completely different type of complex. We have recently been involved[3,4] in the study of macrocycles formed by the template reaction of complexes of tetraamines with nitroethane and formaldehyde, following the work of Lawrance and co-workers.[5-7] It was anticipated that reaction of the cobalt(II) complex of the bridged open-chain ligand *N,N'*-bis(3-aminopropyl)piperazine (L^1) (Scheme 1) might proceed to give cobalt(III) complexes of reinforced[3,4,8-11] macrocycles such as L^2.

Initially an attempt was made to synthesize the cobalt(III) complex ion $[Co(L^1)(NCS)_2]^+$, which could then be treated with formaldehyde and nitroethane to give $[Co(L^2)(NCS)_2]^+$. We have since synthesized cobalt(III) complexes of reinforced macrocycles by a less direct method. This involves synthesizing the macrocyclic ligand using Cu^{II} as the template, followed by removal of the Cu^{II} with sodium sulphide, reaction of the free ligand with Co^{II} and oxidation. However, the attempted synthesis of the precursor, $[Co(L^1)(NCS)_2]^+$, by the initial 'direct' route gave a mixture of dark blue and pale red crystals. The dark blue crystals were presumed to contain the well known tetrahedral $[Co(NCS)_4]^{2-}$ ion, and were not examined further. The pale red crystals however were the typical colour of an octahedral complex of Co^{II}. The IR spectrum indicated that co-ordinated thiocyanate, possibly *N*-bonded, was present in the crystal, as was also the polyamine ligand. The elemental analysis corresponded to the formulation $[H_4L^1][Co(NCS)_6]$. The possibility of an octahedral isothiocyanate complex of Co^{II} led us to carry out the crystallographic study reported herein.



Scheme 1 Proposed synthesis of the cobalt(III) complex of L^2 by the template reaction of the complex of L^1 with formaldehyde and ammonia

Experimental

Synthesis of the Complex.—The ligand L^1 (0.6 g), dissolved in water (6 cm^3) was added to a solution of $CoCl_2 \cdot 6H_2O$ (1.6 g) in water (5 cm^3). Air was passed through this solution for 12 h, and HCl (3.5 cm^3) then added. The volume of the solution was reduced until a crust of dark blue crystals formed. Further crystallisation occurred on standing overnight and the product was recrystallized from dilute HCl. Some of the dark blue crystals (1 g) plus NaSCN (1 g) were dissolved in water (67 cm^3), and air passed through the solution; for 12 h NaSCN (16.7 g) was then added and the volume of the solution reduced to one third. On standing for a week, a mixture of red and blue crystals was deposited. These were filtered off and washed with ice-cold water, which removed the blue crystals , and left only the red crystals (Found C, 31.20; H, 4.45; N, 22.95. Calc. for $C_{16}H_{28}CoN_{10}S_6$: C, 31.40; H, 4.60; N, 22.90%). Two bands assigned as CN stretches in the IR spectrum were observed at 2078 and 2114 cm^{-1}. A very weak band at 779 cm^{-1} was assigned tentatively as the C–S stretch, and a band at 470 cm^{-1} as the N–C–S bend.

Crystallography.—The data were collected at room temper-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Details of the crystallographic analysis of $[H_4L^1][Co(NCS)_6]$

Formula	$C_{16}H_{28}CoN_{10}S_6$
M	611.76
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	7.215(1)
b/Å	8.815(1)
c/Å	21.270(2)
β/°	91.82(1)
U/Å^3	1352.1
Z	2
F(000)	634
D_c/g cm^{-3}	1.50
D_m/g cm^{-3}	1.47(2)
T/K	298
μ/cm^{-1}	10.52
Transmission coefficients	92.73–99.96
θ range/°	3–27
F cut-off	$F > 3\sigma(F_o)$
R'	0.0300
R	0.0372

Table 2 Fractional atomic coordinates (× 10^4) for $[H_4L^1]$-$[Co(NCS)_6]$

Atom	X/a	Y/b	Z/c
Co	0	0	0
N(1,	7 556(3)	293(3)	508(1)
N(2)	1 154(3)	−1 084(3)	804(1)
N(3)	10 869(3)	2 144(3)	376(1)
C(1)	6 958(4)	748(3)	965(1)
C(2)	11 546(4)	−1 452(3)	1 310(1)
C(3)	11 109(3)	3 106(3)	730(1)
S(1)	6 159(2)	1 437(1)	1 615(1)
S(2)	12 137(1)	−1 974(1)	2 034(1)
S(3)	11 467(1)	−5 477(1)	1 232(1)
N(4)	11 698(4)	1 719(3)	2 299(1)
N(5)	4 764(3)	733(2)	4 387(1)
C(4)	12 780(4)	2 333(3)	2 845(1)
C(5)	13 264(4)	1 107(3)	3 316(1)
C(6)	3 846(4)	1 844(3)	3 934(1)
C(7)	5 574(4)	1 563(3)	4 951(1)
C(8)	3 462(4)	−493(3)	4 595(1)

Table 3 Bond lengths (Å) and angles (°) for the complex anion $[Co(NCS)_6]^{4-}$

Co–N(1)	2.114(2)	N(3)–C(3)	1.144(3)
N(1)–C(1)	1.147(3)	N(3)–S(3)	2.802(2)
N(2)–S(2)	2.800(2)	C(3)–S(3)	1.658(3)
N(3)–C(3)	1.144(3)	Co–N(3)	2.139(2)
C(2)–S(2)	1.650(3)	N(2)–C(2)	1.150(3)
Co–N(2)	2.107(2)	N(3)–S(3)	2.802(2)
N(1)–S(1)	2.799(3)	C(1)–S(1)	1.632(3)
N(1)–Co–N(2)	87.5(1)	N(1)–Co–N(3)	86.6(1)
N(2)–Co–N(3)	89.7(1)	Co–N(1)–C(1)	144.9(2)
Co–N(2)–C(2)	165.0(2)	Co–N(3)–C(3)	159.6(2)
N(1)–C(1)–S(1)	178.2(3)	N(2)–C(2)–S(2)	179.3(3)
N(3)–C(3)–S(3)	178.8(3)		

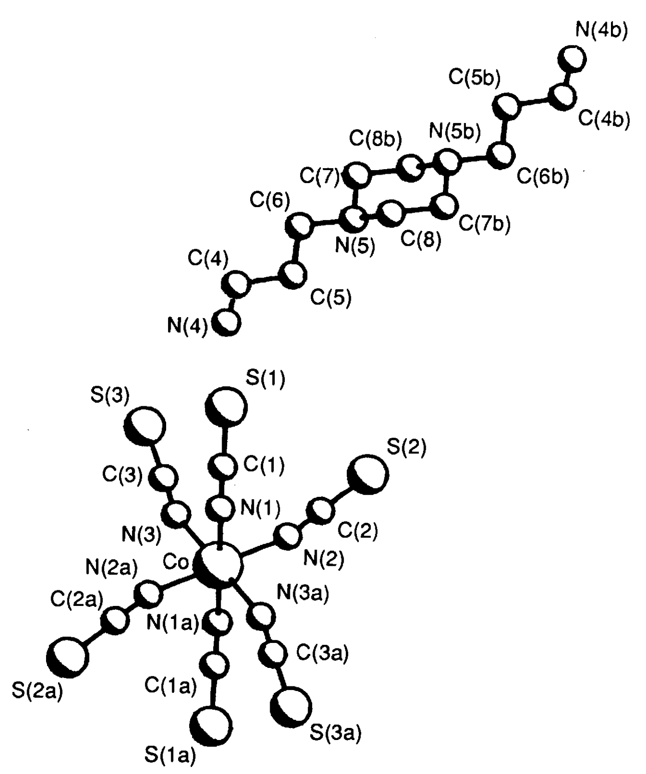

Fig. 1 The structures of the complex anion and cation in $[H_4L^1][Co(NCS)_6]$ with atom labelling

ature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The cell dimensions were obtained from least-squares refinement of 25 high-angle reflections. The ω-2θ scan mode was used with a scan width of 0.6 + 0.35 tanθ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection period. Lorentz-polarization and absorption corrections were applied to the data according to the method of North *et al.*[12] The density of the crystals was determined by flotation on mixtures of chloroform and 1,2-dibromoethane. Crystal data and data collection parameters are given in Table 1. The structure was determined by using Patterson and Fourier techniques with the program SHELX.[13] Fractional atomic coordinates for the structure are given in Table 2 and bond lengths and angles for the complex anion are given in Table 3. A PLUTO[14] drawing of the cation and complex anion is shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The structural study has established the presence of the $[Co(NCS)_6]^{4-}$ ion in $[H_4L^1][Co(NCS)_6]$, as shown in Fig. 1. The average Co–N bond length of 2.11 Å is very similar to that found in the thiocyanate-bridged compound $[CoHg_2(NCS)_6]$.[2] Studies of methanol solutions of cobalt(II) with varying ratios of thiocyanate present[15] indicate the existence of the $[Co(NCS)_6]^{4-}$ ion at high thiocyanate to cobalt ratios, but it has not previously been detected in, or isolated from, aqueous solution.[16] It must be assumed that it is the balance of charge between the tetrapositive cation and the tetranegative anion that leads chiefly to its stabilization in the crystalline state. While Co^{II} yields only the tetrahedral $[Co(NCS)_4]^{2-}$ complex with monopositive cations,[16] the divalent first row transition-metal ions Mn^{II}, Fe^{II} and Ni^{II} yield octahedral $[M(NCS)_6]^{4-}$ ions with cations such as tetraphenylarsonium. It appears that the structure of only the $[Ni(NCS)_6]^{4-}$ ion has been reported thus far.[17] As might be expected from the smaller octahedral ionic radius[18] of Ni^{II} compared to Co^{II}, the average Ni–N bond length in $[Ni(NCS)_6]^{4-}$ at 2.09 Å is slightly shorter than that for the Co^{II} complex.

The bands in the IR spectrum were assigned by comparison with the IR spectrum of $[H_4L^1][CoCl_4]_2$, which allowed for the identification of bands associated with the organic cation. The very weak band at 779 cm^{-1}, absent in the tetrachloro complex, is consistent with N-bonded thiocyanate,[19] as confirmed by the crystal structure.

With hindsight, it is likely that the synthesis reported here is more complex than it need be. The passage of air, which was intended to oxidize Co^{II} to Co^{III}, is probably not required, and there is also probably no need to isolate the blue crystals prior to adding a large excess of thiocyanate. However, the synthesis is certainly reproducible, as on three separate attempts the reported synthesis, with somewhat varying concentrations of reactants, gave the red hexakis(thiocyanato-*N*)cobaltate(II) salt.

Acknowledgements

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